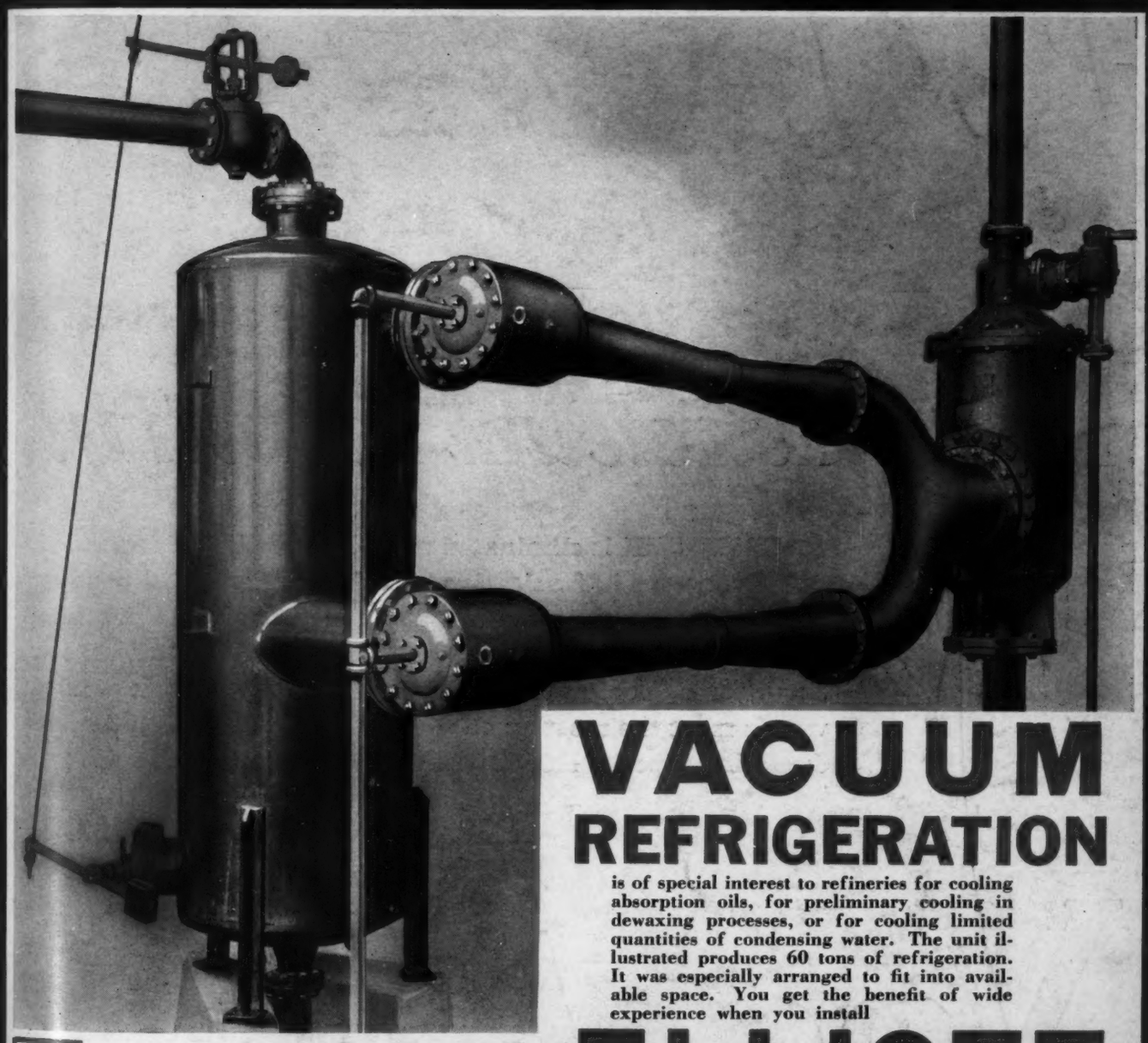

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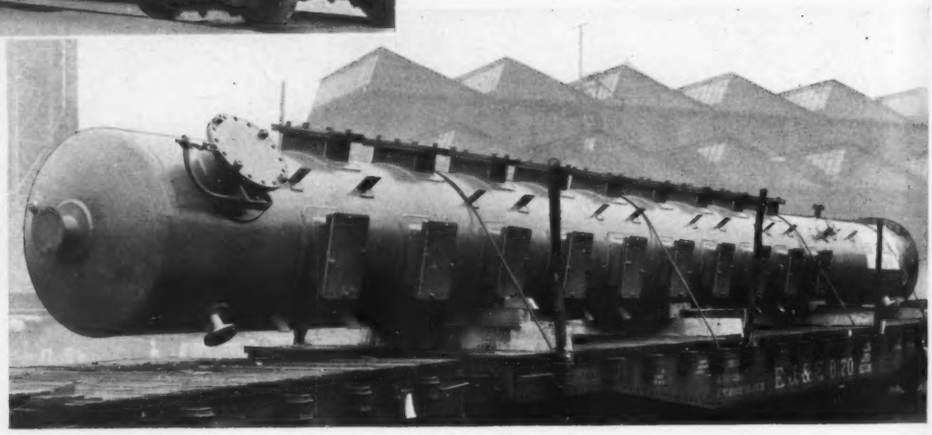

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SEPTEMBER, 1933
Vol. 12, No. 9

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Associate Editor

CONTENTS

Special Features

Code of Fair Competition for the Petroleum Industry . . . . . Special Insert

Competition Under a New Flag 343

Efficiencies Secured in New Three-Column Pressure Distillate Re-Run Unit 344
G. F. Burdick and P. H. Woods

Long Beach Plant Utilizes New Cooling Method 351

The Manufacture of Alcohols and Related Products from Petroleum 353
Dr. Benjamin T. Brooks

Petroleum and Petroleum Gases as Chemical Raw Materials 361
A. R. Bowen and A. W. Nash

Comparison of Cracking and Hydrogenation as Methods of Producing Gasoline 370
R. T. Haslam, R. P. Russell and W. C. Asbury

Regular Departments

Editorial 343

Science and Technology 24a

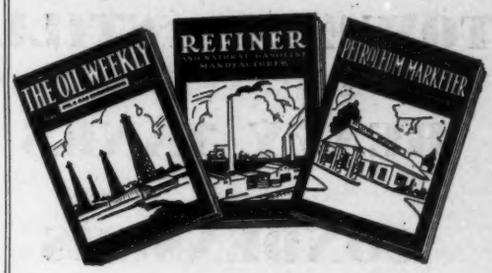
The Month in Review 33a

Plant Activities 36a

New Equipment for the Modern Plant 39a

Items About Manufacturers 44a

Catalogs and Bulletins 45a



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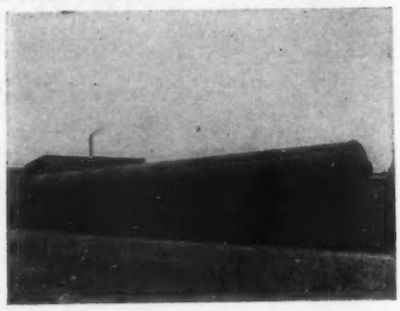

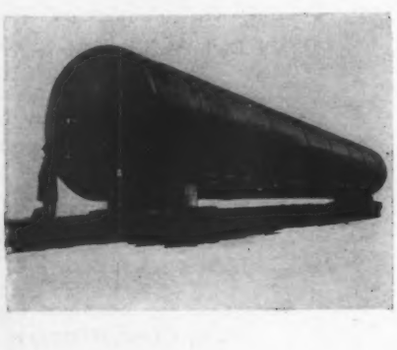

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Competition Under a New Flag . . .

ONE of the follies of youth is to picture the coming of majority as an assurance that obstacles to personal progress will be removed as by a miracle. But the day that brings the privilege of voting does not lessen the effort an individual must put forth to gain a livelihood.

How like youth the petroleum industry awaited the signing of its code! If it could have accomplished half that was predicted or a tenth of what was anticipated the petroleum industry would now be in smooth water and driven by the favorable wind of profit. But the code has been signed and still there is no day without worry.

The code was hailed as an assurance that each refining property in the United States could under its rules operate at a profit. No man ever said or ever believed that true for the industry but he did believe it true of his own property. He knew his competitors could not continue but he knew that he would escape. That individual estimate made a universal estimate for the whole industry.

The rules have been changed but the facts have not. Having too much crude oil, the petroleum industry provided facilities for making more gasoline than was needed. Those facilities still exist and no set of rules can assure profit to unneeded facilities. Under the code each man is going to do what he can to continue his business. The code may be a warning to the individual but he has not seen that phase of it yet. He is still an unhampered individual.

This is no effort to belittle the code. Its brand has burned deep into the surface of the industry and the iron is still hot. If it burns no deeper NRA will be visible for many years.

But the facts thus far reveal dissatisfaction. A substantial part of the industry was confident of price fixing. If that question ever reached the desk of the administrator, it was shoved aside promptly. Consequently the code is an unfinished working instrument and an unsatisfactory document with this substantial wing of the industry. Hundreds of questions are ready for consideration of the planning and coordination committee. Men are waiting for interpretation before they enforce rules. Men read the rules to different conclusions.

So instead of settling controversy and pointing a clear road, the code has brought more controversy and points to a hundred roads. This committee and its regional lesser committees will be answering questions and making interpretations so long as the Code of Fair Competition for the Petroleum Industry exists.

Universal satisfaction will not be accomplished. But individuals and corporations will keep striving to maintain business ventures. The clash of opinions will be accompanied by the clash of business methods.

These are evident now. Both crude oil and gasoline prices have been raised. But several thousand service station owners have not been convinced that 14 cents or 15 cents is the proper price for gasoline. They continue to sell well below those figures. Either they can sell for such prices at profit or they think they can and the effect in either case is identical. Customers are ignoring better equipment, better service and advertising and following the dictates of the pocketbook.

Gasoline thus sold is coming out of refining plants where costs either are lower, the raw material bought below the market or where proper cost records do not exist. There is nothing in the code to prevent a refiner from operating at a loss either knowingly or unknowingly.

If and when the price fixing provision is used, the picture will change. But it will not change the determination to keep properties in operation.

The code has not and never will assure profit to all refining property just as it has not and never will convince any man that his properties are exempt from the elimination that is long overdue. The code is not a peace pact; it is competition under another flag.

Efficiency Secured in New Three-Column

Pressure Distillate Rerun Unit

G. F. BURDICK
Engineer with C. F. Braun & Company, Inc.

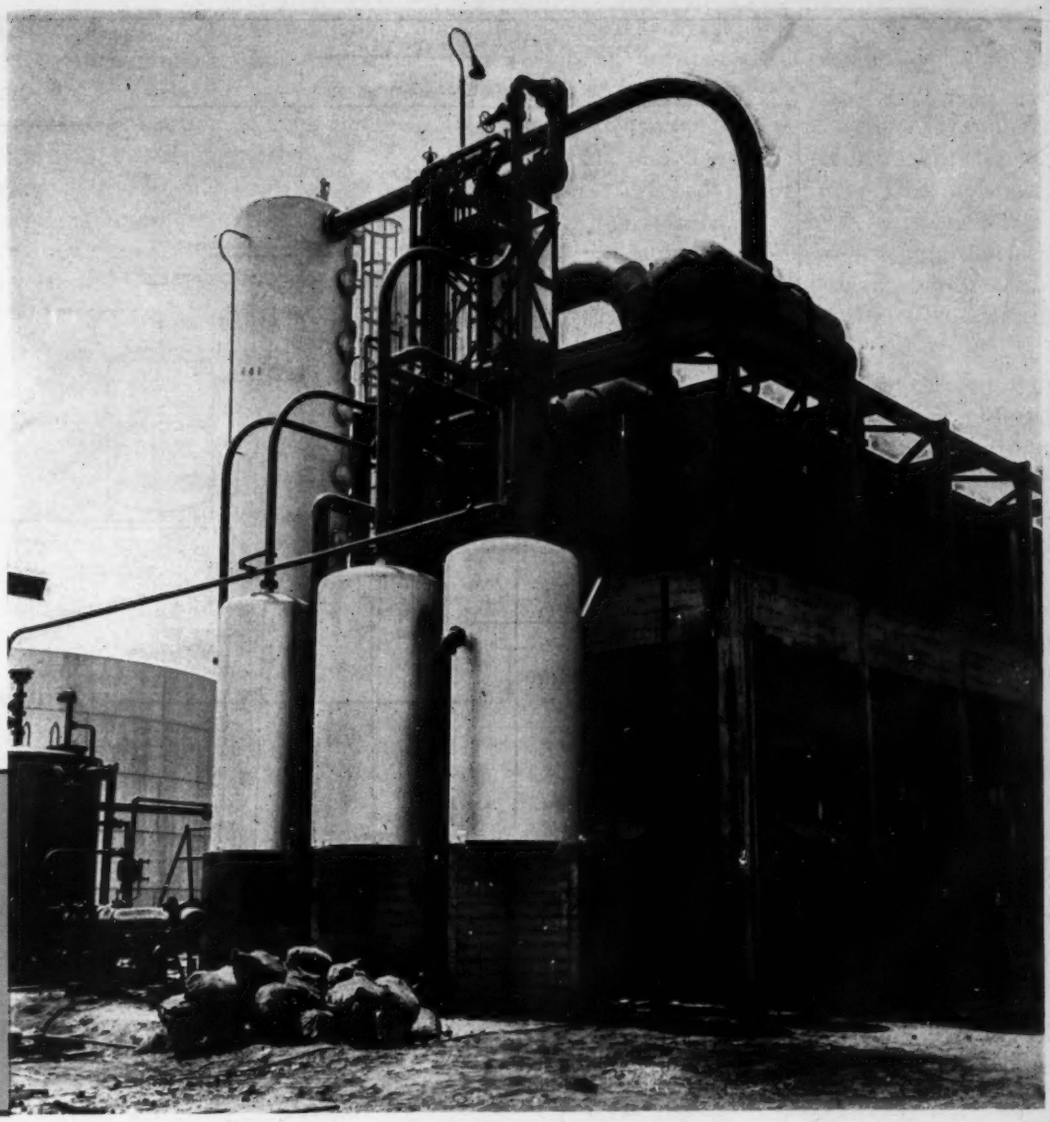
P. H. WOODS
Engineer with Associated Oil Company

PRODUCTION of high-quality gasoline of high anti-knock rating, of stable color, free from sulphur and gums, yet processed at low cost, has long been the refiner's aim. Cracking has produced the anti-knock qualities at low cost, but pressure distillate treating and rerunning costs have been exorbitantly high. The search for a means of reducing rerunning costs led to the development of the plant herein described.

Before going into details of the latest innovation in pressure distillate rerun equipment, a brief review of process development in recent years will be given.

Previous to about three years ago, pressure distillate was rerun to end-point by fractionating in a single bubble-tower operating under atmospheric pressure, as shown in Figure 1. The process was: first, to heat the feed by means of heat exchange with the overhead product and with preheaters; second, to flash and fractionate in the bubble-tower; and, third, to strip the heavy gasoline ends by means of a reboiler in the column base. Steam introduced below the bottom bubble

View of unit from rear showing installation of the three fractionation columns.



Exterior View. Vessels in the foreground are the accumulators.

tray provided the partial pressure effect and completed the stripping action.

The overhead product usually passed first through a partial condenser, counter-current to the pressure distillate feed, then through the water-cooled final condensers, and thence to an accumulator, where the stream was dehydrated of the condensed stripping steam. From this vessel a portion of the product was returned to the top tray of the tower as reflux for end-point control, the balance being pumped to storage.

Heating in the preheaters and reboilers was accomplished either by steam, by recycle hot-oil stock, or by the use of direct fired retorts. In any event, the pressure distillate was subjected to temperatures of at least 330° F., and in the case of the fired heaters, these doubtlessly attained magnitudes of 450° F., or even higher. These excessively high temperatures were distinctly injurious to the stock and demanded a heavy pretreat to remove the compounds that would tend to give trouble when rerunning, and also a heavy after-treat to remove the undesirable products formed at the higher temperatures and thus leave a gasoline a stable color, sulphur- and gum-free.

Large quantities of steam were required to extract all the 420° end-point gasoline from the treated pressure distillate, being on the order of 80 to 100 pounds of steam per barrel of pressure distillate.

Economical production demanded, then, two radical changes: first, a reduction in treating costs; and, second, a reduction in the amount of stripping steam required. To save treating costs the maximum temperature to which the pressure distillate was subjected had to be lowered. With atmospheric distillation, however, an additional amount of steam was required to compensate for the partial pressure effect of stripping. This condition led to the development of the two-stage rerun plant, a combination atmospheric and vacuum unit. The maximum temperature was limited to 275° F., 50 to 75° F. below the minimum level of the single column unit.

Figure 2 illustrates the general flow in the two-column plant. The treated pressure distillate is first pumped, counter-current to the overhead vapors, through the atmospheric partial condenser where it attains a temperature of possibly 180° F. It then passes through preheaters where the effluent temperature ap-

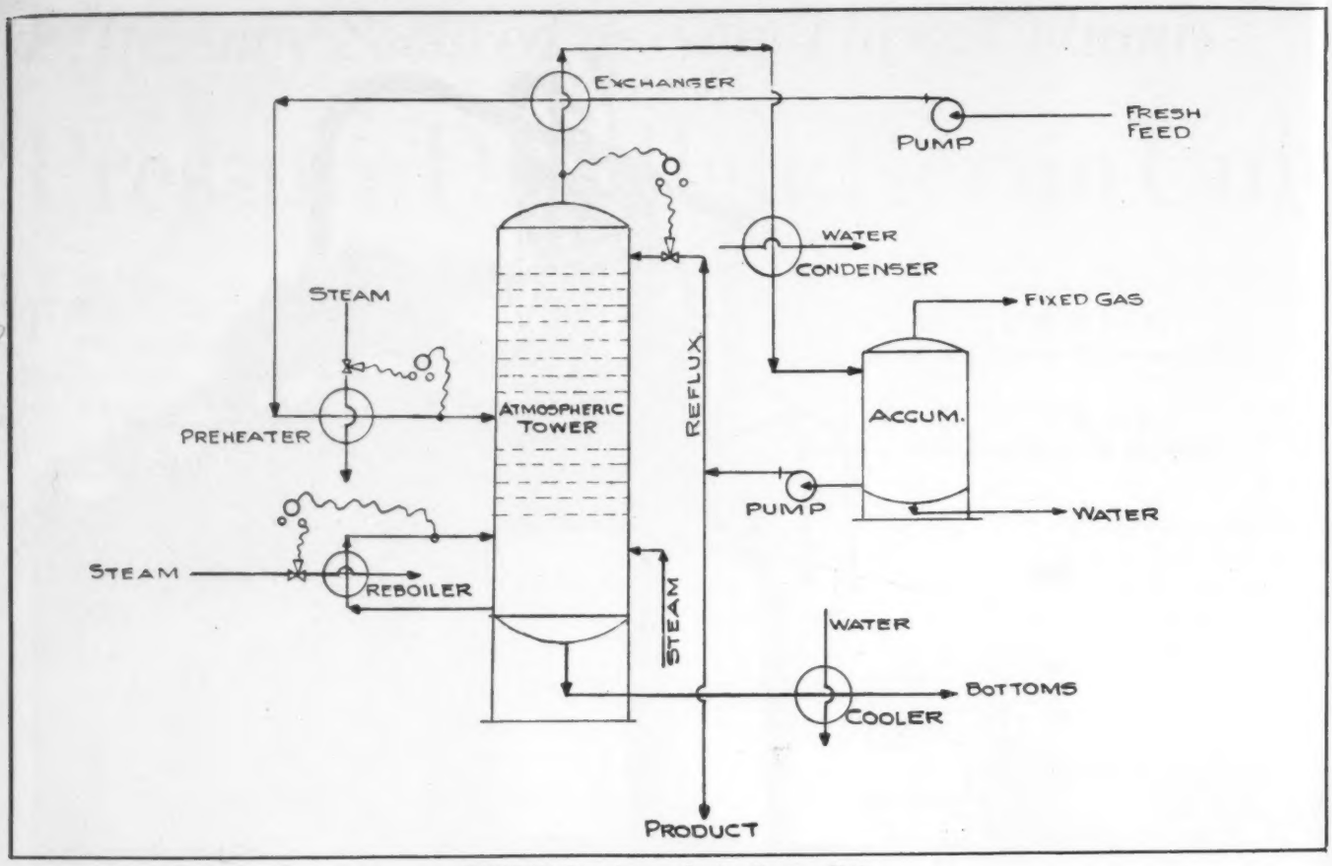


FIGURE 1—*Atmospheric Rerun Unit.*

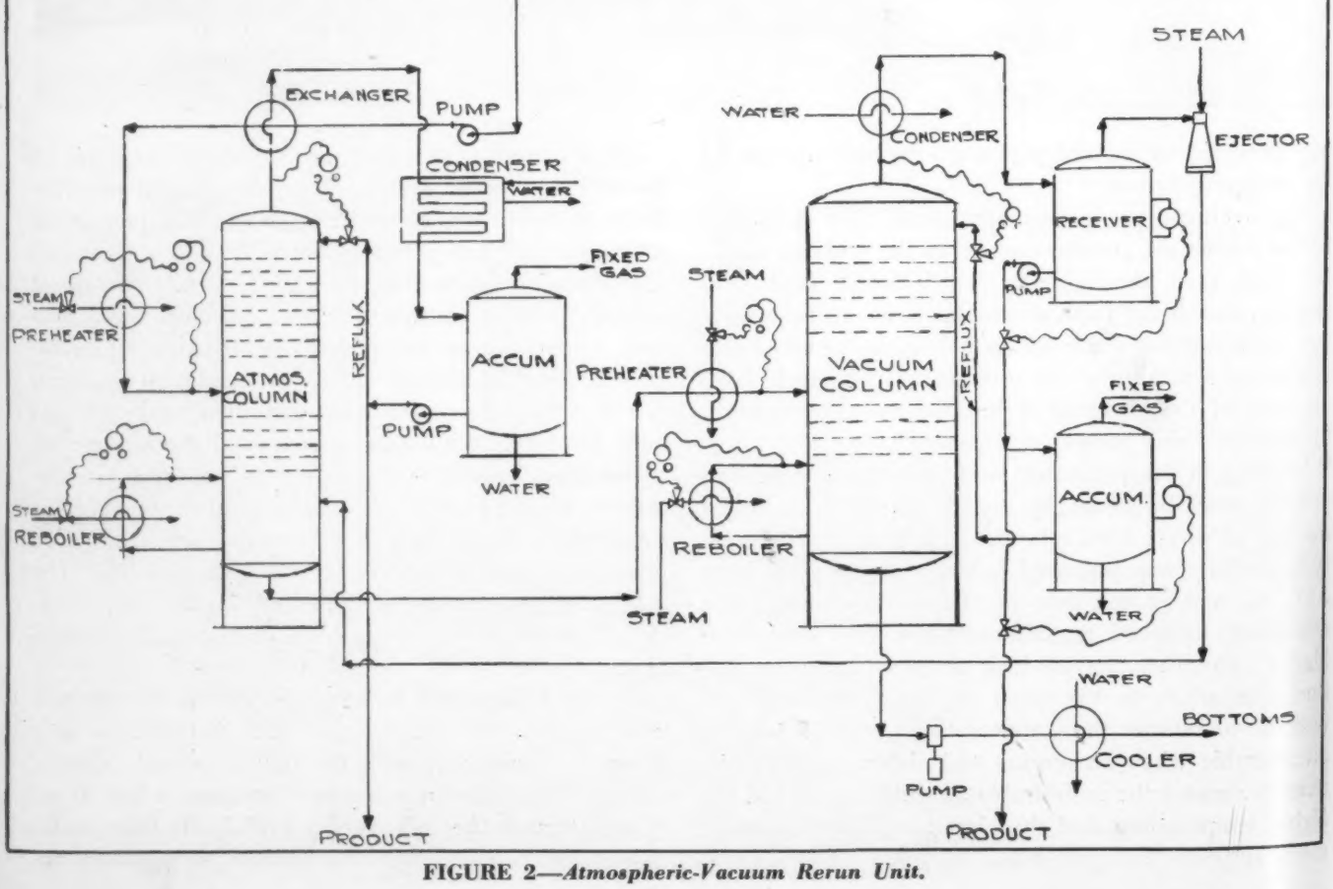


FIGURE 2—*Atmospheric-Vacuum Rerun Unit.*

proaches 250° F. At this level the stream is partially vaporized. It is introduced then into the atmospheric column, where it is flashed. The reboiler in the base of the tower raises the unflashed portion to a temperature of 275° and drives overhead all light ends having a boiling range below 300°-330° F. With atmospheric pressure in the condenser and accumulator these light fractions are readily condensed. A portion of this condensate is used for reflux. No stripping steam is used in the tower.

The bottoms from the atmospheric column, with an initial of about 300° F., are then passed through a preheater wherein a temperature of 275° F., is maintained as the stock is vaporized. It is next flashed in the vacuum column where an absolute pressure of 80 to 100 mm. of Hg. is maintained at the feed tray. A maximum gasoline yield is obtained by the use of a reboiler in tower base and the introduction of stripping steam under the bottom tray. The end-point of the overhead, a heavy gasoline fraction, is controlled by the return of a portion of its condensate as reflux. The vacuum in the tower is maintained by means of steam ejectors.

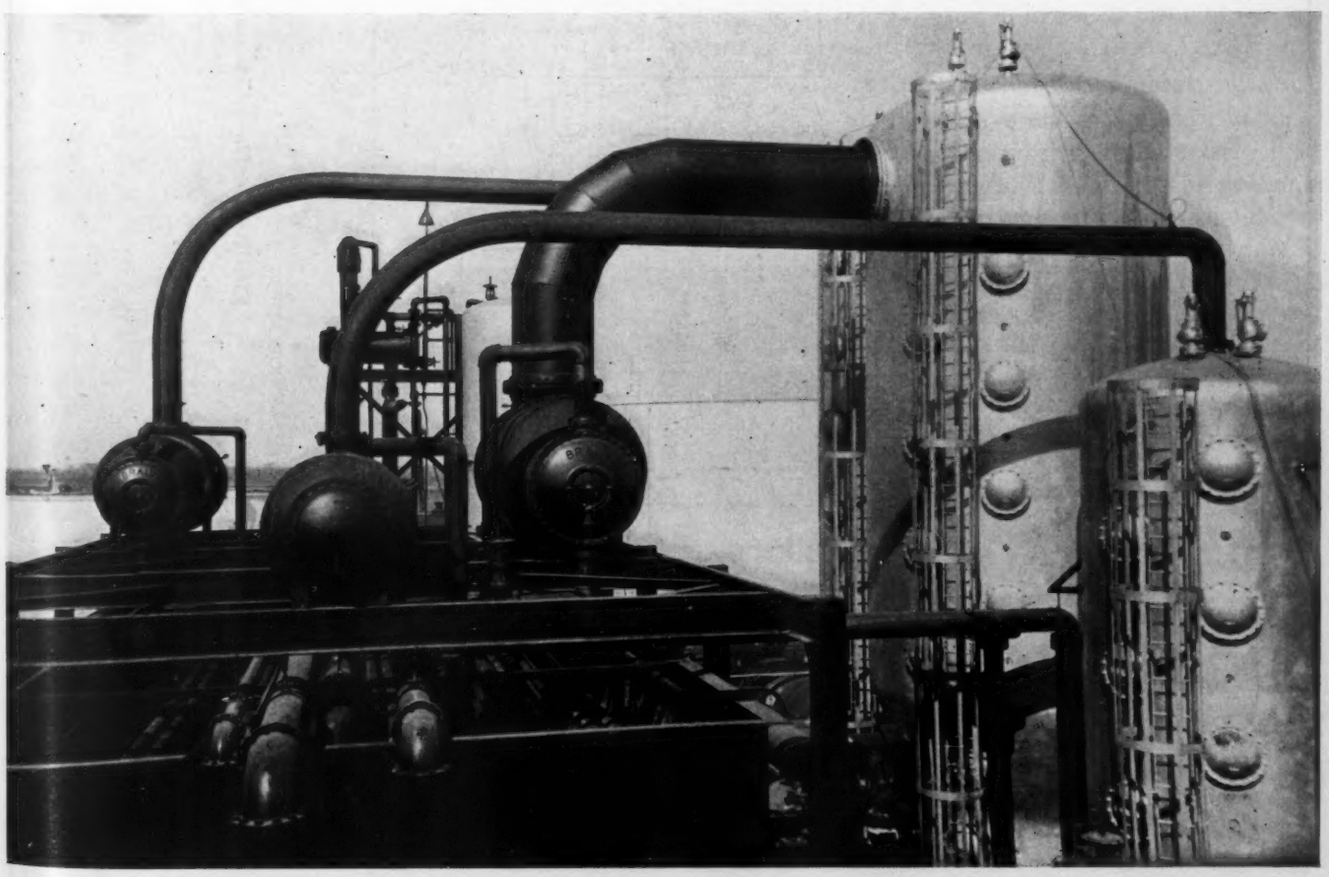
Many such units have been installed throughout this country and their performance has been gratifying. Treating costs have been lowered, mechanical maintenance due to corrosion has been cut in half, and time offstream for cleaning and repairs has been reduced to but a quarter of the time required in earlier plants. And withal, the stripping steam required is but one third that required in the single-column unit. This further results in an appreciable savings in pumping costs for cooling water.

The first step forward was thus made in rerunning pressure distillate and the reduction in manufacturing costs of finished cracked motor fuel. This, however, did not satisfy the refiner. If 275° F. maximum temperature in a two-column atmospheric-vacuum unit can effect such savings in treating and steam, why not extend research further and determine the effects of still lower temperatures?

Trial runs over a two-year period showed that 250° F. maximum temperature still further reduced treating costs and produced a stable 30 color gasoline. These runs were made in two-stage units, however, and, although the treating costs were less, the steam consumption for stripping at 250° F. was considerably increased. The problem very definitely was one of reducing the amount of steam required. Encouraging progress along this line has been made with the unit lately completed at the Avon, California, refinery of Associated Oil Company.

When the company planned to increase cracking facilities early this year, an additional rerun plant was one of the units that became necessary. Decision was made to rerun at not over 250° F., yet it was desired to make the most efficient use possible of stripping steam.

Manufacturing contractors were asked to design and



Vapor lines from towers and condensers over open coil coolers.

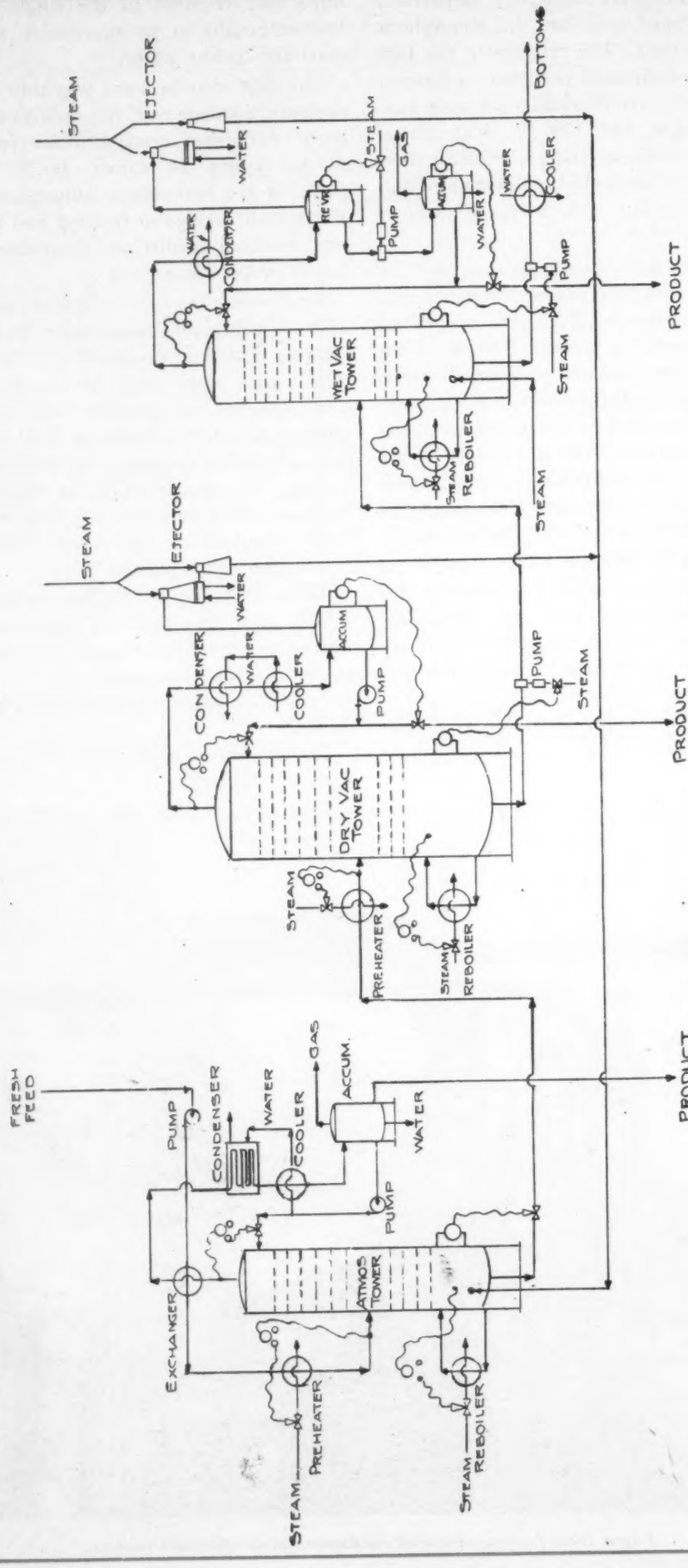


FIGURE 3—*Three-Column Rerun Unit (Patent applied for).*

submit plans for a plant to fulfill the following operating conditions:

A. Charge, 6,000 barrels per 24 hours, treated pressure distillate.

B. Gravity, 56° to 58° A. P. I.

C. Distillation range,

I. B. P.	90° F.
10 per cent	150
50 per cent	285
90 per cent	418
E. P.	480

D. Maximum total overhead product, 97 per cent.

E. Maximum overhead from atmospheric column, 55 per cent.

F. Maximum overhead from vacuum column, 45 per cent.

G. Maximum bottoms from vacuum column, 15 per cent.

H. Bottoms to contain not more than 5 per cent gasoline of 420° F. End-Point when fractionally distilled under an absolute pressure of less than 20 mm. of Hg.

I. Maximum temperature at any point within the system not to exceed 250° F.

The plant which was constructed was from the plans developed and submitted by C. F. Braun & Company, Inc., Alhambra, California. The unit is now in operation and has surpassed the rather stringent requirements. Moreover, the stripping steam required is only one third to one half that necessary in a two-column unit operating at 275° F., and but a small percentage of that required in a single-column plant operating at 360° F. Application has been made for letters patent covering the design.

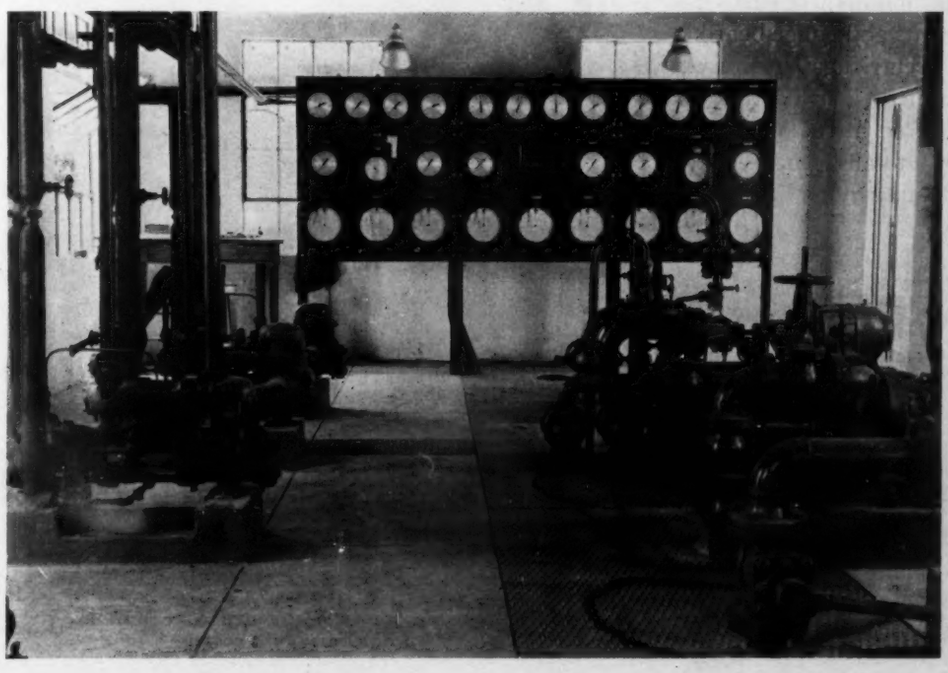
This installation consists of three columns, and is shown diagramatically in Figure 3. The first is an atmospheric tower, the second is a dry vacuum tower, and the third is a wet vacuum tower. All have fractionating and stripping trays with removable reboilers below the bottom trays.

The pressure distillate is pumped, as in a two-column unit, through a partial condenser on the atmospheric column, where it extracts part of the heat load from the overhead product and reflux and attains a temperature of 180° F. This charge passes on through a vertical steam preheater where the temperature is further raised to 230° F., and about 45 per cent is vaporized as it enters the atmospheric tower. It is further stripped by means of a steam heated reboiler in the column base. Exhaust from the vacuum-column ejectors supplies the small quantity of stripping-steam.

The overhead product of light gasoline gives up part of the heat load to the incoming charge in a vapor-to-feed exchanger. It is completely condensed in cast-iron pipe-coils in a 22 x 40 x 10-foot condenser box. Final cooling within 3° F. of the water temperature is done in tubular coolers. The condensing system offers less than one pound pressure-drop. The end-point of the overhead product is maintained by pumped-back reflux.

The bottoms from the atmospheric column, 45 to 50 per cent of the feed, expands through preheaters where the temperature is maintained at 250° F. and where about 60 per cent is vaporized. The bottoms now partly in vapor form enter the dry-vacuum column, and all the remaining gasoline except the heavy ends are taken overhead. No stripping steam is used in this column, but a reboiler in the base maintains 250° F. temperature. Efficient stripping is done by running at low vacuum.

The small quantity of bottoms from this dry-vacuum column enter the wet-vacuum tower and are maintained at 250° F. The reboiler supplies the necessary heat, both sensible and latent. A small quantity of stripping-steam taken from a pump exhaust, supplies the partial-



Interior of pump-house showing control instrument panel and part of the unit pumps.

pressure effect. Reflux returned to the top tray maintains the end-point.

The overhead product, the reflux, and a small quantity of stripping-steam is condensed in a Braun domed-type low-pressure-drop condenser. Elliott two-stage ejectors maintain vacuum on both the dry and wet vacuum columns.

The bubble-columns, accumulators, separators, and tanks are electrically welded, Class 2, ASME, pressure-vessels with one-eighth-inch corrosion allowance. Sixteen-inch manholes give free access to all compartments.

Efficient fractionation is largely a matter of hydraulic design. And further, the accurate frabrication of trays, caps, gas-risers, and down-pipes is indispensible. The trays in this unit are adjustable for level and heavily ribbed to eliminate buckling. The caps and gas-risers are stream-lined to reduce friction, and are of heavy cast-iron to withstand corrosion.

Reboilers in the column bases are readily removable for inspection and cleaning. So are the tube bundles in the preheaters, condensers, partial-condenser-exchanger and coolers. Temperature strains are eliminated by floating head construction.

Salt water is used for cooling, and to withstand its corrosion effect, Admiralty tubes are used in partial condensers, in vacuum-column condensers, and in all coolers. For the atmospheric-column the condenser consists of cast-iron tubes submerged in salt water in the welded-steel box which is mounted on top of the pump house.

The pump house is of reinforced concrete and hollow tile with steel sash and doors. This building houses all motors, pumps, instruments and gauge board.

Centrifugal pumps are of United Iron Works make, all-iron fitted, and are driven by totally-enclosed, 1750 r.p.m. motors. These consist of:

I. Charge Pump.
II. Gasoline-to-storage pump.
III. Spare for I and II.
IV. Dry vacuum overhead and reflux pump.
V. Reflux-to-atmospheric-column pump.
VI. Spare for IV and V.

Steam pumps are Dean Brothers Simplex, iron-fitted, and consist of:

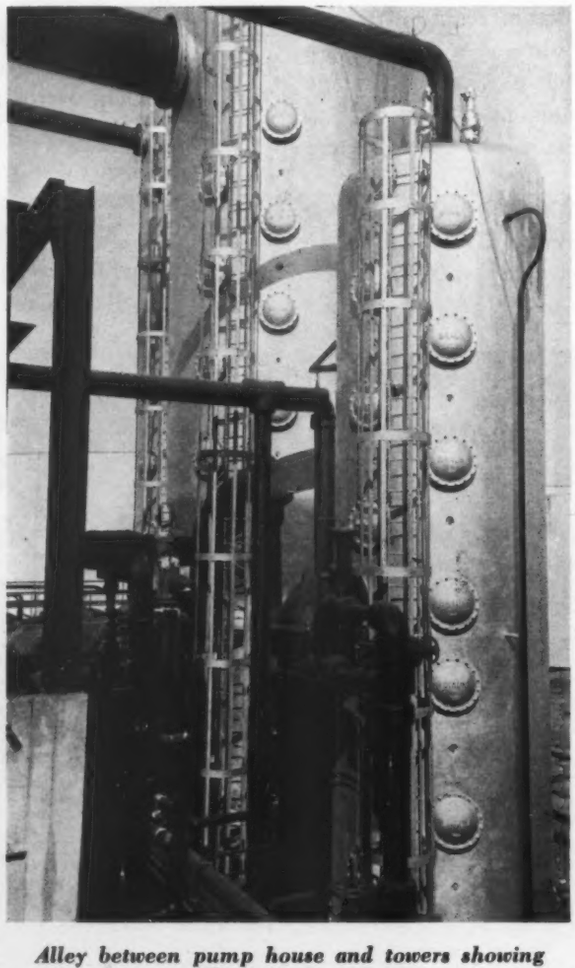
VII. Wet vacuum-column feed pump.
VIII. Wet vacuum-column overhead and reflux pump.
IX. Spare for VII and VIII.
X. Wet vacuum-column bottoms pump.
XI. Spare for X.

The temperature recorder-controllers are Foxboro Stabilog. They give close regulation over wide operating ranges and eliminate hunting. The vacuum recorders are Bristol absolute-pressure gauges and give true absolute pressures with varying barometric pressures. All instruments and gauges are flush-mounted on black Bakelite board. The safety valves are high-capacity nozzle-type. The springs are enclosed by bonnets and provided with lift levers. The trim is alloy steel.

Electrical controls are magnetic oil-switches in series with safety disconnects. Push buttons are located near the motors in the pump house. The switches are in a central distribution house 250 feet from the plant site.

The plant occupies a square but 40 x 40 feet, a compact unit, yet ample operating space surrounds all pumps, motors, switches, controls, columns and tubular equipment.

The chief advantages of this three-column unit are five. First, low temperature operation results in lower treating costs. Second, stripping-steam is saved because a very small quantity of pressure distillate is stripped in the wet-vacuum-column. Third, cooling water and its pumping is saved because the reflux and steam quantities condensed are small. Fourth, heating steam in reboilers is reduced because the amounts of reboil material in conjunction with reflux is small. These last three items alone, not considering treating costs, represent a yearly saving of about $15,000. Fifth, a wide range of flexibility is obtained, which is of particular advantage when making a product of narrower boiling range, such as aviation gasoline.



Alley between pump house and towers showing preheaters on towers.

Long Beach Plant Utilizes New Cooling Method

CHANGING conditions in the Los Angeles Basin, Southern California, as in the Mid-Continent area, have brought about the necessity for a more thorough fractionation of natural gasoline. In November, 1932, Gilmore-Dabney Gasoline Company installed a modern fractionating column and accessories designed and fabricated by C. F. Braun & Company in its No. 3 plant in the Long Beach field.

This plant is producing approximately 20,000 gallons of finished gasoline per day from a raw gas load of about eight million cubic feet of gas. This gas comes from the closely spaced wells in the Long Beach field and the Signal Hill district. Clark 200-horsepower gas injection engines are employed to bring in the gas and compress it.

One feature has been introduced in this plant which differs from most other plant construction, and that is the manner in which the compressed gas cooling coils are arranged. Each pair of compressor cylinders is provided with separate cooling units for the discharged gas. Discharging into a line common to both cylinders, the gas enters this cooling unit before joining that compressed by the other cylinders in the compressor room. Ordinarily the reverse has been the practice in the Mid-Continent and other parts of the country, the gas leaving the cylinders and immediately entering a common header and then entering the bank of cooling units as it continues to the absorbers.

With the application of this idea of separate cooling units, the louvre tower basin or sump has been divided into as many compartments as there are cooling coils serving the compressors. Concrete dividing walls extend from each side of the sump and reach the floor, forming water-tight compartments which may be drained separately, but with common drains leading to the suction line of the water circulating pumps. These drains are all equipped with gates that may be closed independently of the others. This feature commends itself for one reason in particular, for instance when cleaning out the louvre tower sump with the large pit, it is almost necessary to shut down the plant to remove the sediment, leaves, accumulated sand and sludge, whereas with the separate compartments, it is only necessary to shut down the individual engine, and ordinarily that is only done when some mechanical adjustment must be performed. While the mechanics are busy with the engine, other employes open the drains permitting the water to drain from the compartment and a hose attached to a pump forcing a strong pressure of water, it is played on the floor, thus removing the sludge. Water can be cut off from the tower covering this section and consequently the employes are not subjected to falling water.

The distillation and absorption operation carries a load of 470 gallons of mineral seal oil per minute, running 84 gallons per thousand cubic feet of processed gas. This oil enters the absorbers at a temperature of 76°F. with an outlet temperature of 90°F. From the exchangers, the oil enters the stripper or still at 342°F. with a system pressure of 54 pounds. The knock back or dephlegmator is carried at 206°F. to maintain the desired end point, and water flowing to the dephlegmator runs around 70°F., requiring very little at that temperature to accomplish the desired results.

After the gasoline has been condensed and recovered in the accumulator tank, it automatically drains away to the raw storage tank, from which it flows constantly to the surge or supply tank at the fractionation apparatus. Worthington close clearance simplex steam-driven pumps, 8 x 4 x 12 inches were installed with which the gasoline is handled in the first stage of fractionation. This raw natural gasoline is naturally very wild. With the over-all circulation of mineral seal oil such as employed at this plant, certain amounts of the lower boiling fractions not desired in a finished product are condensed and thrown into the surge tank. An analysis of the raw product shows the following characteristics:

	Mol %	Weight %	Liquid Vol. %
Methane	0.13	0.03	0.05
Ethane	0.81	0.30	0.45
Propane	10.65	5.81	7.30
Iso-Butane	7.64	5.51	6.34
N-Butane	28.18	20.30	22.38
Iso-Propane and Heavier	52.59	68.05	63.57
A.S.T.M. Distillation			
Recovery	79.0	Specific Gravity @ 60/60	0.646
Residue	1.0	A. P. I. Gravity	87.5
Loss	20.0		
	100.00		

Discharging at a column pressure of 185 pounds, the pumps drive the raw gasoline first through a pair of Braun heat exchangers, then into the column proper just above the eighteenth plate. The column is Braun, 36 inches in diameter by 57 feet in height with the reflux condensers placed in a rack built above the top of

the column. Following the course as in other towers, the gasoline is partially stripped of the lower boiling fractions as it falls through the stripped plates to the base, from which it flows by gravity to the reboiler.

Braun equipment is used for the reboiler operation and a temperature of 266°F. is maintained on the stream by admitting live steam through a Neilan reduction valve which maintains a constant pressure of 31 pounds. A Neilan controller is set on the instrument panel which controls the temperature by the admission of more or less steam as the occasion requires. This instrument remotely controlling the 1½-inch valve, handles steam at a boiler pressure of 150 pounds before reduction to the Braun reboiler.

To provide for a more even fractionation of the raw gasoline, it was found that by having the shells of the reflux condensers insulated, the temperature as shown on the Neilan recorder would be a straight line. We found from past experience that with the shells operating bare, the change in atmospheric conditions from a hot day to the cool night would make an appreciable difference in the quality of the bottom product. An almost constant condition is the result of the insulated condensers, the water entering at an average of 76°F. with the outlet averaging 131°F. The volume is measured and shows that this plant circulates 259 gallons of water per minute over the reflux condensers.

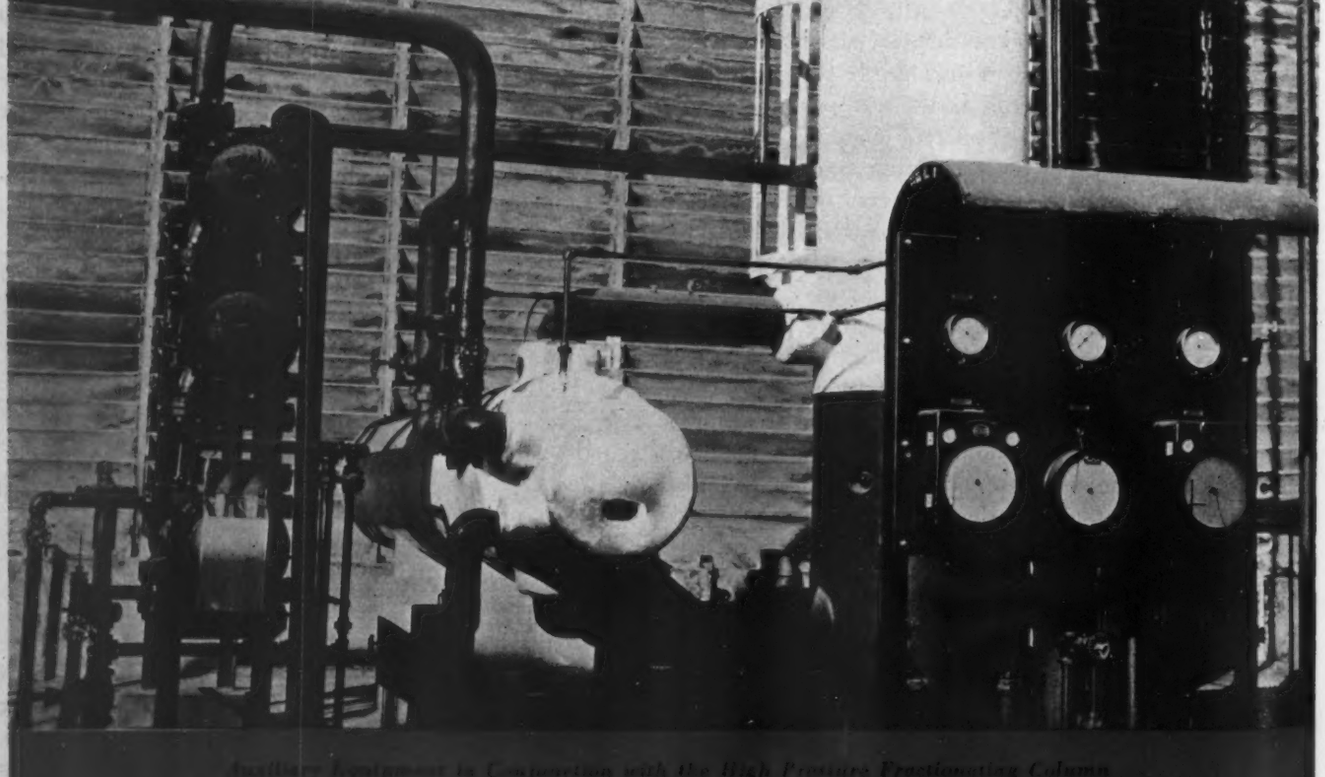
Gasoline is trapped from the rear of the reboiler through the operation of a N. G. E. float cage operating a Wilgus one half-inch valve. This valve is sufficiently large to remove the gasoline in sufficient quantities to prevent an accumulation in the tower and reboiler. A sample removed from the after-coolers shows the following characteristics:

	Mol %	Weight %	Liquid Vol %
Propane	0.25	0.13	0.16
Iso-Butane	10.23	6.99	8.18
N-Butane	30.92	21.10	23.66
Iso-Pentane and Heavier	58.60	71.78	68.00
A.S.T.M. Distillation			
Recovery	91.5	Specific Gravity @ 60/60	0.675
Residue	1.0	A. P. I. Gravity	84.0
Loss	7.50		
	100.00		

As the characteristics of the raw feed to the column runs practically uniform, the operation of the column, after it has been placed in equilibrium is also constant, taking off as an overhead product the following:

	Mol %	Wt. %	G.P.M.
Methane	0.38	0.14	?
Ethane	9.30	6.51	?
Propane	88.70	91.16	?
Iso-Butane	1.00	1.37	0.326
N-Butane	0.62	0.82	0.195
Gravity of sample, 1.475 (air — 1.0)			

No attempt has been made to refractionate the overhead into a liquefied fuel product and it is expanded directly into the plant stripped-gas lines which feed back to the field and to the domestic and industrial fuel distributing systems.



Auxiliary Equipment in Connection with the High Pressure Fractionating Column

The Manufacture of

Alcohols and Related Products From Petroleum

DR. BENJAMIN T. BROOKS

THE paper forms a general survey of the literature, patent and otherwise, dealing with the separation and conversion into alcohols and the corresponding ketones, of olefines obtained either as by-products in cracking operations or by the cracking of the lower paraffins.

There are two main sections; the first deals with the production, concentration, separation and purification of the lower olefines, while the second describes their conversion into alcohols chiefly through the agency of sulphuric acid, the effect of catalysts, the properties of the alcohols and finally of the acetates and ketones derived therefrom.

After an extensive review of the literature dealing with the concentration of ethylene by such methods as activated charcoal, cooling and compression, absorption in oil, etc., the conclusion is reached that for the production of ethyl alcohol it is doubtful whether any useful purpose is really served, as the gas is readily removed by 95 per cent sulphuric acid at 60-80° C. even in concentration as low as 2.5 per cent.

Actual separation of the individual olefines from the gases containing them is undoubtedly accomplished most successfully by the use of sulphuric acid, although different writers show considerable variation in the pressures, temperatures and strengths of acid used. Catalysts increase the rate of absorption but tend to increase polymer formation. Gas oil mixed with the acid definitely increases the efficiency of the scrubbing operation.

The necessity for the removal of sulphur compounds from the olefines is emphasized, although the resulting unpleasant odor of the alcohols when this is not done is an advantage if it is proposed to use them as denaturants. Alcohols containing sulphur compounds may be purified by oxidation.

The preparation of ethyl, isopropyl, butyl, amyl and hexyl alcohols from the appropriate olefines and sulphuric acid is discussed together with the properties and products of the corresponding acetates. The conversion of secondary alcohols into the corresponding ketones by means of a brass catalyst at 500-800° C. is mentioned and the properties of the ketones obtainable given.

This paper was read before the World Petroleum Conference, London, England, July 19-25, 1933.

IN recent years the synthetic products made from petroleum, or oil gas, have been manufactured in a high degree of purity. This has been due to the large amount of research done and also to the perfection of physical methods of separating pure raw materials. The alcohol esters and particularly the ketones have established themselves in the nitro-cellulose lacquer industry and the manufacture of synthetic ethyl alcohol, of high purity, has been established on a large scale during a period of unprecedented low molasses prices. Ethylene glycol, ethanolamines and ethylene oxide, all chemical curiosities prior to 1921, have found important commercial uses. Acetone, heretofore obtained by fermentation and wood distillation, is cheaply made from isopropyl alcohol. Both synthetic ethyl alcohol and isopropyl alcohol, the latter blended with 35 per cent of synthetic methanol, has invaded the anti-freeze market, which has for many years been much the largest commercial use for ethyl alcohol. With more assurance of an abundant supply of petroleum than geologists and oil producers of an earlier day would have thought possible, the production of ethyl alcohol and other solvents from petroleum at much lower costs than they can be made by fermentation of molasses or grain appears to be assured for some time to come, particularly in view of the fact that most of the raw materials, ethylene, propylene, butenes, etc., are now produced in quantity as by-products incidental to large refinery operations.

Important as these chemical developments are, from the standpoint of their magnitude and economic soundness, the great volumes of petroleum and its major products which are now annually produced are more than ample to produce all of the common organic chemicals and solvents now known, which could conceivably be made from petroleum, without interfering with the adequate supply of the present refinery products. It is hardly conceivable that the manufacture of all the organic chemicals and solvents which could possibly be made from petroleum could affect the petroleum price structure. In the long run it will be the price of coal which will set the upper limits to the value of petroleum.

The first consideration in any case of industrial synthesis is the cost of raw material. Without going into the matter in detail, the price statistics for the last 10 years, for gasoline, kerosene and gas oil for localities in the Mid-Continent area are given in Figure 1. Refined paraffin wax (125-127°) was quoted in 1932 (New York) at 2⅞ cents per pound, crude petrolatum at 1¾ cents. Cracking still gases are commonly burned as refinery fuel or sold at a slight advance over their fuel value. Statistics of production for most refinery prod-

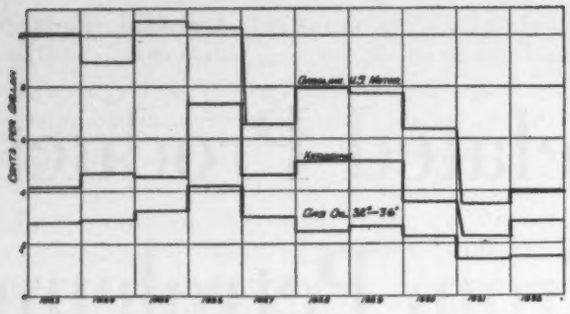


FIGURE 1
Average Yearly Price, Group 3

ucts are not very significant in this connection, since any of them could be greatly increased in amount if the demand existed. Thus the consumption of liquefied gas, butane and propane, in 1932 was 33 million gallons, but the amount potentially available at existing gasoline recovery plants is reported to be about 13 million gallons *per day*. Crude petrolatum has little demand and its production is rapidly increasing; it is commonly thrown into cracking still charging stock.

Some of the factors which have held back the chemical utilization of petroleum are:

(1) The complexity of petroleum oils and the difficulty of separating pure products, either as raw material or from the reaction products.

(2) Widely varying nature of crude oils from different fields.

(3) Lack of chemical knowledge of all except the simplest petroleum hydrocarbons.

The industrial developments, along chemical synthesis lines, to date have naturally been based upon the simple chemistry of the hydrocarbons from methane to the hexanes. Very little new chemistry has been required by these developments, but in so far as the processes are industrially new it has generally been possible to surround them with apparently adequate patent protection.

Most of the important chemical developments have been fitted into existing refinery operations. One company producing a series of alcohols and related derivatives utilizes the by-product still gases produced by a pressure cracking operation. Another company producing ethylene glycol and ethyl alcohol uses the by-product gas from the Gyro vapor-phase cracking process. Thus the utilization of the uncondensed cracked gases, formed incidental to cracking for gasoline (the principal product), bears much the same relation to petroleum refining as the manufacture of coal tar light oil and its derivatives does to the coking of coal.

OIL GAS

Although oil gas has long been known, its production at low cost was hardly possible prior to the perfection of vapor-phase or high-temperature cracking processes in recent years. The old Pintsch gas retorts were very inefficient and were operated over a wide range between maximum and minimum temperatures. Close temperature regulation, particularly in high-temperature cracking, was appreciated by W. A. Hall,[1] one of the pioneers of oil cracking, and this feature was greatly perfected by Luis De Florez,[2] the inventor of a cracking apparatus adapted to vapor phase operation. During the World War the Hall process was operated at high temperatures for the conversion of petroleum to benzole. In the Hall process cracking at 605° C. gave 17.7 per cent gas containing 49-50 per cent olefines; at 725° C. 66 per cent of the oil was gasified, the gas containing 40 per cent total olefines.[3]

J. E. Zanetti[4] first showed that in small laboratory apparatus propane and butane give a maximum of about 38 per cent total olefines at 750° C. While many laboratory studies of the decomposition of propane have been made, the results of W. J. Podbielniak are of industrial interest since the process was operated on an industrial scale. Podbielniak[5] obtained a maximum ethylene yield at about 815° C. (1500° F.). One volume of commercial propane gives about 1.8 volumes of cracked gas containing 26-28 per cent ethylene. The apparatus developed by Podbielniak for the analysis of such cracked gases has been of great service in the chemical use of such gas.

The thermal decomposition of methane and ethane to produce ethylene is of little or no industrial interest. As regards methane as a raw material the catalytic effect of various materials was noted by Slater,[6] but Stanley and Nash[7] have shown that any catalytic material favors the final equilibrium mixture of methane, carbon and hydrogen. F. Fischer[8] states that under the most favorable experimental conditions methane yields 13 per cent of liquid hydrocarbons. Stanley and Nash confirm Fischer's results and state that a typical reaction gas, obtained by very brief reaction time contained acetylene 1.33 per cent, ethylene 1.11 per cent, ethane 0.10 per cent. Most of the work on the pyrolysis of methane has been with the object of producing a crude benzole motor fuel, or hydrogen for hydrogenation.[9]

The pyrolysis of ethane has repeatedly been investigated. Pease and Durgan[10] found 20.3 per cent ethylene in the equilibrium mixture at 650° C.

It is well known that the yields of gas obtainable from gas oils vary somewhat. In the data of gasoline production by vapor-phase cracking published by C. R. Wagner[11] it is shown that the per cent of charging stock gasified is 28 to 35 per cent, or 1100 to 1300 cubic feet per barrel. When the olefine gases are desired, as for chemical synthesis, the gas yield can be considerably increased, as will be evident from the results shown in the following Table I. In common refinery practice three Gyro cracking units product about 5,500,000 cubic feet per day. The De Florez[12] cracking process is not commonly operated under high temperature or vapor-phase conditions, but is flexible and can be so operated when desired.

TABLE 1
Oil Gas Yields[13]

No.	Temp., °C.	Gas per 42 gal. Oil, Cu. Ft.	Olefines, %	REMARKS
1	743	2990	36.6	Experimental apparatus
2	743	2867	33.7	" "
3	743	3136	33.5	" "
4	785	3320	27.3	" "
5	782	3365	27.7	" "
6	682	2490	35.8	Penn. gas oil
7	760	2968	30.1	" "
8	700	2520	36.5	Russian gas oil
9	800	2870	46.2	Experimental, oil 0.847
10	850	3255	43.1	" " 0.807
11	650	1887	43.6	Experimental
12	750	2884	30.6	"
13	593	1260	45—48	Gyro gasoline mfr.
14	595	1090	45—48	" "
15	598	1175	45—48	" "

Two typical analyses of Gyro gas, as made under normal refinery conditions of cracking, mainly for gasoline, are as shown in Table 2.

TABLE 2
Composition of Gas by Gyro Process

	I. % by vol.	II. % by vol.
Carbon dioxide and hydrogen sulphide	0.89	0.28
Methane and hydrogen	29.6	28.5
Ethylene	23.1	23.1
Ethane	12.8	11.1
Propylene	13.3	15.7
Propane	4.9	4.4
Butenes and butane	8.3	10.1
Pentenes and pentanes	4.1	4.0
Above pentenes and pentanes	3.9	3.1
Total olefines	47.2	48.4

The quantity of available olefines produced by a typical vapor-phase cracking plant, yielding 4500 M gas per day is as follows: ethylene 40.4 tons, propylene 38 tons, butenes 29.9 tons, amylenes 19.7 tons, hexenes and gasoline 15.5 tons (about 5000 gallons).

An important advance aiding in the production of pure synthetic products has been the perfection of fractional distillation methods for separating close-cut hydrocarbon fractions. Thus it has been possible to separate on a large scale a butene fraction of 98.5 per cent butenes, containing not over 1.5 per cent C_3 and C_5 hydrocarbons, and a liquid C_3 fraction of like purity. W. W. Clough and C. O. Johns[14] have described a series of industrial alcohols of a high degree of purity. In the first industrial production of glycols a mixture of ethelene and propylene, derived from oil gas, was used yielding a mixture of ethylene and propylene chlorohydrins and glycols.[15] By separating the two olefines the two series of derivatives are now manufactured in pure condition. In the first industrial attempt to make ethyl ether from the ethylene in oil gas, P. Fritzsche removed the higher olefines by scrubbing the gas with concentrated sulphuric acid. Fritzsche made no attempt to produce alcohols, and all of the olefines in the gas other than ethylene were converted to oily polymers or tar. Fritzsche[16] was also handicapped at that time by the fact that vapor-phase cracking of oil under carefully regulated and uniform conditions had not been developed.

CONCENTRATION OF OLEFINES FROM CRACKED GASES

The first industrial production of ethyl alcohol from ethylene sought to utilize the ethylene in coal gas. It was natural, therefore, that processes for the concentration of ethylene should be proposed. F. Soddy[17] patented the use of charcoal for this purpose, but Bury and Ollander[18] state that in their work on coal gas charcoal absorption was tried, to obtain a gas rich in ethylene, but abandoned. Berl and Smidt[19] have given quantitative results for the absorption of ethylene in activated carbon. They saturated 100 g. carbon with 12.4 litres of a gas mixture, 10 per cent ethylene and 90 per cent methane, and on heating to carbon obtained a gas containing 50 per cent ethylene.

The process of Claude[20] for the purification of the hydrogen of coal gas, liquefies the ethylene and part of the methane at —140° C. According to F. Valette[21] and P. Damm[22] the Claude liquefaction process is employed at Bethune, France, obtaining an ethylene fraction 20 to 30 per cent ethylene. The Soc. Anon. d'Explosifs et Prod. Chimique[23] employ both pressure and cooling to separate a series of liquid fractions from oil gas: (1) pentenes and pentanes, (2) butenes and butane, (3) propylene and propane and (4) ethylene and ethane. G. Curme[24] absorbs the low-boiling hydrocarbons in oil, and the oil solution, containing the dissolved volatile components and gas, is progressively warmed as it flows downward through a tower. A rectification effect is produced, in the presence of the solvent, the latter permitting the rectification to be carried out at more moderate pressures and temperatures than is possible without the solvent. Voorhees and Youtz[25] concentrate ethylene by utilizing its greater solubility in 95 per cent ethyl alcohol, as compared with methane and ethane. They recommend scrubbing oil gas containing about 35 per cent ethylene and propylene under a pressure of about 150 pounds, releasing the pressure and optionally heating the alcohol, to give a gas containing 75 to 85 per cent olefine content. It has long been known that mercury salts combine with olefines and may thus be separated from inert diluents. The original olefines may be recovered by decomposition of the mercury salts.[26] Processes have been described using silver salts for the same purpose, but are believed not to be used industrially.

It is very doubtful if there is any practical utility, so far as synthetic ethyl alcohol is concerned, in concentrating ethylene. Bury and Ollander,[27] using coal gas, found that with reasonably good surface contact between the acid and the gas 71 per cent of the 2.5 per cent ethylene in the gas could be absorbed in two minutes, by 95 per cent sulphuric acid at 60-80° C. This is confirmed by Tidman,[28] who states that 80 to 90 per cent of the ethylene in such gas can be absorbed in three minutes under the same conditions. Saunders[29] describes a liquefaction method, carried out under 15 to 20

atmospheres pressure and temperatures as low as *minus* 70° C., for separating a liquid propylene fraction from oil gas, but an American company operating under the patents of C. Ellis[30] and his co-workers have been manufacturing isopropyl alcohol on a large scale for several years, from cracking still gas. The use of an absorbent oil, together with sulphuric acid, greatly increases the efficiency of the process.

SEPARATION OF OLEFINES BY ACID TREATMENT

Fritzsche (*loc. cit.*) removed the ethylene homologues from oil gas by concentrated sulphuric acid at temperatures below 40° C. The C. Still[31] Company removed most of the higher olefines and some of the propylene by compressing the gas to 100 to 200 atmospheres and then scrubbing the gas with 50° Be. sulphuric acid, undoubtedly a cleaner and more economical process than that of Fritzsche. C. Ellis[32] first removes propylene by treating with sulphuric acid of sp. gr. 1.80 at low temperatures followed by stronger acid at temperatures above 60° C. Isham and Born[33] treat oil gas containing ethylene, propylene and butenes successively with separate lots of concentrated sulphuric acid at increasing temperature stages, the last absorber containing fresh concentrated sulphuric acid at 90° C. Taveau[34] claims the treatment of oil gas with progressively increasing concentrations of sulphuric acid. It has long been known that isobutene is much more reactive to dilute mineral acids than the normal butenes, readily yielding tertiary butyl alcohol.[35] Similarly, trimethylethylene is much more reactive than the isomeric amylenes and may be selectively removed from olefine mixtures to form tertiary amyl alcohol.[36] This feature is included in a process of separately producing tertiary and secondary butyl alcohols, and tertiary and secondary amyl alcohols, close-cut butenes and amylene fractions being successively treated, first with dilute acid to form the tertiary alcohols and then with stronger acid to form the secondary alkyl sulphates and alcohols.[37] Hydrochloric acid has been suggested for the same purpose but has not been adopted in industrial operations.

PURIFICATION OF OLEFINES

It was early recognized by C. Ellis that hydrogen sulphide should be removed, as well as mercaptans, or the resulting alcohols contain mercaptans. The presence of the malodorous mercaptans in isopropyl alcohol when used for denaturing ethyl alcohol has been considered desirable by the U. S. authorities. However, isopropyl alcohol free from malodorous impurities and suitable for the manufacture of perfumes is regularly manufactured. The higher alcohols, acetates and ketones used in the manufacture of lacquers are also manufactured free from sulphur and other malodorous impurities. When the hydrocarbon gases are separated into close-cut fractions and the hydrogen sulphide removed the resulting alcohols are of excellent quality with respect to odor. In general, alcohols containing mercaptans as impurities may be purified by oxidation of the sulphur compounds.[38]

It is well known that high-temperature cracking produces small proportions of dienes. When these are present in substantial proportions they are polymerized in the sulphuric acid treatment with the liberation of considerable heat and the formation of high-boiling hydrocarbon polymers. In the close-cut butene fraction, made by cracking at about 1100° F., the butadiene content is about 12 to 14 per cent. This diene can be selectively removed by treating the hydrocarbon mixture in the cold with a saturated solution of cuprous chloride, the butadiene being subsequently liberated from the acid cuprous chloride compound by heating to about 55°-60° C.[39]

ETHYL ALCOHOL

A litre of ethyl alcohol, said to have been made from ethylene in coal gas, was exhibited at the London Exhibition of 1862.[40] If true, it was in the nature of a "stunt" and of no industrial significance. The early industrial work of P. Fritzsche has already been mentioned. It is of interest, in view of the patent to J. Compton,[41] that Fritzsche[42] noticed the beneficial effect of the presence of ethyl sulphuric acid in promoting the absorption of ethylene by the acid solution.

This effect was also noticed by S. G. Plant and N. V. Sidgwick[43] and by the Cie. Bethune.[44]

Synthetic ethyl alcohol, as made from properly purified oil gas, is purer than ethyl alcohol made from fermentation. A small proportion of ethyl ether is normally obtained, this by-product constituting a new industrial source of this material.

The issued patents resulting from the industrial work in Europe and America deal with special improvements in the process of manufacture. The Skinningrove Iron Company[45] describes the preliminary removal of hydrogen sulphide, drying the gas by 80 per cent sulphuric acid, treating the gas counter-current with 95 per cent sulphuric acid at 60° to 80° C., dilution of the acid mixture and distillation of the alcohol. The claims of the patent, however, are limited to certain heat exchange principles.

Catalysts have been proposed to promote the absorption of ethylene by the acid. Damiens[46] mentions a score of elements alleged to have a catalytic effect, but in a later patent he claims only cuprous oxide[47] or cuprous salts, in 66° Be. sulphuric acid and at 15° to 50° C. Damiens states that dilution of the resulting acid mixture with 60 per cent of its weight of water and then distilling gives 22 per cent of ether to 78 per cent of alcohol; by diluting with 140 per cent of water only four per cent of ethyl ether to 96 per cent of alcohol is obtained. The same writer states that although the addition of silver or mercury salts gives rapid ethylene absorption in 95.5 to 99.5 per cent sulphuric acid at 60° C., hydrocarbon polymers mainly are formed. Engelhardt and Lommel[48] have patented the use of silver salts in sulphuric acid for this purpose. Glund and Schneider[49]

have shown that, using 94 per cent sulphuric acid and one-half per cent silver nitrate, the rate of absorption at 20° C. is about equal to the rate for acid alone at 80° C.; at 40° C. the rate with the catalyst is three times the rate of acid alone at 80° C. However, catalysts are not necessary for efficient absorption.

K. P. McElroy[50] suggested a general process in which olefines were circulated through hot dilute acid, and more recently a process has been described in which a mixture of ethylene and steam are passed through dilute acid, 60 to 85 per cent sulphuric acid at temperatures up to 200° C. The maximum conversion to ethyl alcohol is reported as 1.39 per cent.

The opinions so freely expressed in the older literature, that the cost of the sulphuric acid consumed and the cost of reconcentrating it is too great for the economic manufacture of ethyl alcohol, may possibly have been correct for processes such as that of Fritzsche, but the manufacture of oil gas under efficient, controlled conditions, the purification of ethylene, the development of industrial uses for the other constituents of oil gas (see below), the advances made in the art of concentrating sulphuric acid and the high efficiencies attendant upon the formation of large proportions of diethyl sulphate, have greatly changed the picture.

S. G. Plant and N. V. Sidgwick (*loc. cit.*) noted the formation of diethyl sulphate in substantial proportions at 70° C. Starting with fresh acid they noted a continuous acceleration in the rate of absorption until finally the rate decreased as the proportion of diethyl sulphate increased. H. R. Curme[51] has patented a method for producing diethyl sulphate by volatilizing the ester out of the acid mixture, with the stream of excess gas and recovering it from the gas. C. Maimeri[52] also describes a method for producing diethyl sulphate by absorbing ethylene in sulphuric acid, 80 to 100 per cent, at 65° to 75° C. under a pressure of 15 atmospheres; the diethyl ester was precipitated by the addition of water and separated. The use of pressure markedly increases the absorption rate; a pressure of 500 pounds per square inch or more, with acid concentrations of 80 to 95 per cent at 80°-95° C., are recommended.[53] Under these conditions diethyl sulphate is rapidly formed until about 70 per cent of the theory for two mols. of ethylene have been absorbed, when the rate rapidly decreases. Pressure up to 50 atmospheres are also recommended in a recent patent[54] in which the use of acid concentrations within the range 50 to 80 per cent is claimed. Similar conditions but with pressures up to 250 atmospheres are described in a later patent to the same company.[55] C. A. Basore has shown that ethyl hydrogen sulphate is slowly hydrolyzed and states that at 110° C. the hydrolysis is complete in about 50 minutes, and recommends 50 to 70 per cent by volume of water for dilution. He describes the use of an autoclave to effect the hydrolysis.

ISOPROPYL ALCOHOL

The industrial manufacture of isopropyl alcohol from the propylene in cracked oil gas by C. Ellis, M. D. Mann and their associates was the pioneer development in the field of synthetic alcohols. This alcohol closely resembles ethyl alcohol in its physical properties and solvent value. It is produced mainly in three grades, crude for denaturing purposes, 91 per cent and anhydrous; a product suitable for perfumers' use is also manufactured. It is more easily dehydrated than ethyl alcohol; a brief digestion with caustic soda and subsequent distillation give the anhydrous alcohol distilling at 82.4° C.

The physical properties of pure anhydrous isopropyl alcohol are as follows:[56]

Melting Point	—85.8° C.
Boiling Point	82.4° C. at 760 mm. dt/dp = 0.033° C. per mm.
Vapor Pressure	32.4 mm. of Hg at 20° C.
Density	(20°/4° C.) 0.7887 (0.7283 at b.p.)
Viscosity	(20° C.) 0.02431 poise.
Flash Point	11.7° C. (53° F.) (Closed cup.)
Refractive Index (nD)	1.37925 at 15° C. 1.37757 at 20° C.
Critical Temperature	234.9° C. 1.3749 at 25° C.
Critical Pressure	53 atmospheres.
Latent Heat of Vaporization (at B.P.)	160 cal./gm.
Heat of Combustion	7970 cal./gm.
Specific Heat (cal./gm./°C.)	0.563 at 0° C., 0.677 at 30° C., 0.740 at 50° C.
Surface Tension (20° C.)	21.7 dynes/cm.
Dielectric Constant (20° C.)	26.
Vapor Density	2.127 at 100° C.

The properties of the azeotropic mixture with water are as follows:

Composition	91.1 per cent alcohol by volume, 87.7 per cent by weight.
Boiling Point	80.4° C. at 760 mm.
Specific Gravity	20°/4° C. 0.8157. 60°/60° F. 0.8190 (6.82 lb./gal.)
Refractive Index	1.2765 at 20° C.
Viscosity	0.02106 at 25° C.
Flash Point	64° F. (closed tester).
Coefficient of Expansion	0.001062 per degree C.

Isopropyl alcohol forms a large number of binary azeotropic mixtures of which the following may be noted:

Other Component	Wt. % Isopropyl Alcohol	Boiling Point of Mixture, °C.
Carbon Bisulphide	0.8	44.6
Chloroform	4.2	60.8
n-Hexane	22	61
Isopropyl Ether	10	64.9
Carbon Tetrachloride	18	67
Cyclohexane	33	68.6
Cyclohexene	36	71
Benzene	33.3	71.92
Ethylene Dichloride	45	74
Trichlorethylene	28	74
Ethyl Acetate	23	74.8
Methyl Ethyl Ketone	30	77.3
Isopropyl Acetate	52.3	80.1
Toluene	69	80.6
Tetrachlorethylene	80.6	81.7

Some of the more important uses of isopropyl alcohol are as follows:

(a) *Anti-freeze Solution.*—The alcohol is a satisfactory anti-freeze solution, miscible in all proportions with water, and free from the offensive odor of completely denatured ethyl alcohol, as approved by the U. S. authorities, for use in automobile radiators. Where freezing temperatures below 0° F. are encountered, a mixture of 65 per cent isopropyl alcohol and 35 per cent methyl alcohol, which gives the equivalent protection,

per unit volume of alcohol, as ethyl alcohol, is recommended. The freezing point (initial freezing) of the two common anti-freeze alcohols, 95 per cent ethyl and isopropylmethyl blend are given in Figure 2.

FIGURE 2

It should be pointed out that Dr. R. R. Sayres, surgeon of the U. S. Public Health Service, has recently issued a report stating that there is no health hazard in the reasonable use of methanol for such purposes. The use of 10 per cent wood alcohol, the most toxic form of methyl alcohol, has been practiced generally for many years without harmful results. Due to American prohibition regulations, completely denatured ethyl alcohol must be denatured with materials which impart both a very disagreeable odor and taste. A special impure grade of isopropyl alcohol purposely made to contain malodorous impurities (mercaptans) is made for denaturing purposes, but the isopropyl alcohol sold for anti-freeze use is free from objectionable odor.

(b) *Dehydrating Agent.*—The alcohol, easily obtained in the anhydrous condition, is useful for the dehydration of nitro-cellulose, especially for export purposes, where a tax or duty on ethyl alcohol is a consideration. It may also be used for drying and preserving animal and vegetable tissues, for drying sugars, starches, proteins, etc.

(c) *Denaturant.*—Officially approved for formulas 39, 39 A and 40 of the U. S. Bureau of Internal Revenue.

(d) *Surgical Antiseptic.*—Isopropyl alcohol has superior bactericidal power, as compared to ethyl alcohol, according to Dr. D. H. Grant.[57] The most effective concentrations are 30 to 50 per cent.

(e) *Solvent.*—Compared with ethyl alcohol of the same concentration, isopropyl alcohol generally has a slightly greater solvent power for essential oils, waxes, esters, etc. It may be used generally where a neutral alcoholic solvent is commonly employed, as in the extraction and purification of alkaloids, glucosides, etc.,[58] recrystallizing organic products such as ethyl *p*-aminobenzoate, acetylsalicylic acid, resorcin, etc. According to J. W. Poole[59] this alcohol is superior to acetone in the dewaxing of petroleum distillates.

The replacement of ethyl alcohol by isopropyl alcohol in the perfume industry has been noted by several writers.[60]

Much of the isopropyl alcohol now manufactured is converted into acetone and the acetate, the former competing with acetone made by fermentation, and the ester replacing ethyl acetate in many industrial uses.

In 1876 Berthelot[61] obtained a small amount of isopropyl alcohol from the propylene in coal gas, by treating the gas with sulphuric acid and hydrolizing the acid product. By saturating concentrated sulphuric acid with propylene and diluting the product he obtained di-isopropyl sulphate which could be slowly hydrolyzed to the alcohol.[62] Fritzsche observed the formation of a small proportion of isopropyl alcohol when the acid product of his preliminary scrubbers was hydrolyzed and distilled. In 1920 C. Ellis[63] published an account of the industrial manufacture of isopropyl alcohol from cracking still gas. Since this time an extensive patent literature has developed on this and other alcohols which it is not necessary to mention in detail.

The conspicuous improvements in the art are the use of an absorbent oil with the acid which permits efficient utilization of lean gas at low pressures, hydrolysis of the diluted acid product[65] prior to distillation, careful control and skill in operating the process and proper design of apparatus employed, based upon experience.

G. O. Curme[66] and H. S. Davis[67] recommended the use of 100 per cent sulphuric acid for the absorption of propylene. It is difficult, however, to avoid excessive polymerization under these conditions, even with generous refrigeration. Curme's patent is directed primarily to the hydrolysis of the di-isopropyl sulphate produced.

BUTYL ALCOHOLS

Secondary butyl alcohol, or butanol-2, is the raw material for the manufacture of secondary butyl acetate and methyl ethyl ketone. Tertiary butyl alcohol, a chemical curiosity made only by difficult synthesis, has been produced in quantity and employed as a solvent, as a raw material to produce the iso-octane employed as a standard anti-knock engine fuel, as a raw material for synthetic musk, etc.

W. W. Clough and C. O. Johns[68] have described pure butanol-2 made from the butenes of cracking still gases. The light cracked gasoline or butene fraction, when

treated with 65 per cent sulphuric acid, with cooling, readily yields an acid extract which on dilution yields tertiary butyl alcohol.[69] Although the literature notes that tertiary butyl alcohol is decomposed by *N*/50 normal mineral acids, the alcohol may be satisfactorily distilled from 40 per cent sulphuric acid solutions, if rapidly distilled with steam through acid-proof vitreous columns.[70]

The selective removal of butadiene has been referred to in the preceding, in connection with the separation of olefines. It is of interest to note that butadiene, like isoprene, can be polymerized to a rubber. By condensing with maleic anhydride good yields of tetrahydrophthalic anhydride can be obtained, as shown by Diels and Alder,[71] and that a series of new high-boiling esters similar to the di-alkyl phthalates[72] already familiar in the lacquer industry can be made. The diethyl ester boils at 133° to 137° C. at five mm., the dipropyl ester boils at 140° to 141° C. at five mm., the dibutyl (normal) ester boils at 186° to 192° C. at 18 mm. and the secondary diamyl ester boils at 163° to 165° C. at five mm. This interesting anhydride can also be condensed with glycerine and glycols to a new series of hard transparent, nearly colorless resins similar to the well-known glyptal resins.[73] The economic utilization of butadiene is intimately connected with the utilization of the olefines which accompany it in highly cracked petroleum products.

When the butenes are properly purified, as by the successive removal of isobutene and butadiene, the remaining butenes can be successfully sulphated under a fairly wide range of conditions. C. Ellis and M. J. Cohen (*loc. cit.*) have claimed broadly the treatment of mixtures of olefines of cracked petroleum with sulphuric acid of less than 1.84 specific gravity. A. T. King[74] recommends sulphuric acid, 78 per cent, and C. Weizmann and D. A. Legg,[75] who apparently were interested in converting normal butanol to secondary butanol through the normal butenes, recommend the use of 75 per cent acid. R. Taveau[76] uses 85 per cent sulphuric acid for this purpose, at temperatures below 30° C., and a recent patent to W. Engs and R. Z. Moravec[77] uses 90 to 100 per cent sulphuric acid to produce mainly dibutyl sulphate. Apparently very pure butenes and carefully regulated conditions are necessary in the latter process. On the other hand, normal butenes may be converted to butyl hydrogen sulphate with very little polymerization by treating in the liquid phase under pressure with sulphuric acid 60 to 70 per cent at temperatures of 30° to 40° C.[78]

AMYL AND HEXYL ALCOHOLS

The early literature notes the conversion of "amylenes," made from amyl alcohol, in part to tertiary amyl alcohol.[79] There appears to be no commercial use for the tertiary amyl alcohol, which, however, is not producible in large proportion from cracked petroleum amylenes. The amyl alcohol made by the acid treatment of cracked petroleum amylenes consists chiefly of pentanol-2 with small proportions of pentanol-3. The laboratory preparation of secondary hexyl alcohols was described by Wanklyn and Erlenmeyer,[80] who used sulphuric acid of about 80 per cent concentration. They noted that on dilution with water part of the material appeared as free hexyl alcohol and part remained as hexylsulphuric acid which could be hydrolyzed to hexyl alcohol, a general behavior of alkyl sulphate mixtures on dilution. S. R. Merley[81] has observed that the separation of secondary hexyl or other higher alcohols helps the removal of hydrocarbon polymers from the diluted acid product.

Secondary amyl alcohols are used chiefly in the form of acetates as solvent in the lacquer industry and for the manufacture of methyl propyl and di-ethyl ketones, the latter being one of the newer commercial developments in the lacquer solvent field.

Very pure secondary amyl alcohols made from petroleum amylene do not have the pungent, choking odor of fusel oil, and the secondary acetates also have a milder, less pungent odor than amyl acetate made from fusel oil. The boiling point of the alcohol is about 118° to 119° C. and the specific gravity is 0.8088 at 20°/4° C.

ACETATES

The acetates of isopropyl, secondary butyl and secondary amyl alcohols are used in the nitro-cellulose lacquer industry and for other industrial purposes. Of these the amyl acetate is the most valuable. The physical properties of these acetates are as shown in Table 3.

TABLE 3
Physical Properties of Alcohol Acetates

Alcohol	Isopropanol	Butanol-2	Butanol-2, 85%	Pentanol-2	Pentanol-2, 85%
B.p., °C.	88.7	112.2	108—114	133—135	128—135
Sp. Gr. $\frac{15°}{0}$	0.8732	0.8760	0.861—$\frac{15}{15}$	0.9222—$\frac{}{4}$	0.863—$\frac{15}{15}$
Lbs. per gal.	7.287	7.3105	7.17	—	7.18
$N\frac{20°}{D}$	1.3735	1.3882	—	—	1.4021
Az. mixture plus water, % ester by vol.	91.0	84.5	—	74.5	—
Az. mixture plus water, B.p., °C.	80.5	87.0	—	92.0	—

The secondary alcohols are very readily acetylated, the method of Buc and Clough[82] being particularly adapted to the esterification of secondary butyl and amyl alcohols. In both cases ester containing 12 to 15 per cent of the alcohol has a greater solvent power for nitro-cellulose than the pure ester. These acetates are stable and show no tendency to hydrolyze with water or moisture at ordinary temperatures.

The process of directly combining olefines with anhydrous acetic acid, with a little sulphuric acid catalyst, does not give satisfactory yields of ester with normal butenes and amylenes, when carried out at ordinary temperatures as originally proposed for the terpenes by

Bertram and Wahlbaum.[83] Better yields are obtained when the reaction mixture is heated.[84] The olefines yielding tertiary alcohols such as isobutene and trimethylethylene give the highest yields of ester, and at room temperature, but H. S. Davis and C. C. Harford[85] specify their removal before treating the residual butenes and amylenes with acetic acid.

KETONES

Until the development of processes for the manufacture of secondary alcohols from olefines and the manufacture of the corresponding ketones, these excellent pyroxylin solvents were not available in quantity. Small quantities only have been available in the acetone oils. J. G. Park and H. E. Hofmann[86] have called attention to these solvents and their value in solvent compositions for lacquers. Some of the physical properties of these ketones, including acetone, are given by them in Table 4.

TABLE 4
Physical Properties of Aliphatic Ketones

	Acetone	Methyl Ethyl Ketone	Methyl Propyl Ketone	Methyl Butyl Ketone	Methyl Amyl Ketone
Molecular weight	58	72	86	100	114
B.p., 760 mm., °C.	56.1	79.6	102	127.2	150.2
Sp. Gr. $\frac{20°}{4°}$	0.7915	0.8050	0.8089	0.8209	0.8269
Ref. ind. $\frac{20°}{D}$	1.3587	1.3791	1.3895	1.4024	1.4110
Vap. press., 20°C.	184.8	77.5	30	10	3.6
Flash point,* °C.	—16.7	— 7.2	7.2	22.8	41.1
Latent heat, cal./gm.	125	106	91	83	83
Surf. tension, 20°C.	23.7	24.6	25.2	25.5	—

*Closed cup.

All of the above ketones have pleasant ethereal odors. While acetone and methyl-ethyl-ketone have been known and used industrially for some time the three higher homologues are industrially new. Methyl-ethyl-ketone containing a small proportion of ethyl alcohol is a good solvent for practically all grades of cellulose acetate. The higher ketones are not good solvents for cellulose acetate, but are latent solvents when used in conjunction with certain solvent plasticizers. The cellulose ethers are soluble in all of the above ketones. These ketones are also excellent solvents for nitro-cellulose judged both from the viscosity of the nitro-cellulose solutions and their tolerance for hydrocarbon diluents. They are miscible in all proportions with the other solvents and diluents used in the lacquer industry.

All four of the higher ketones are excellent solvents for linseed and tung oils, ester gum, kauri, Manila, pontianac, glyptal type resins, amberols, cumerons, vinyl acetate resins, rosin, nitro-cellulose and ethyl cellulose. For further details regarding evaporation rate, blush resistance, etc., the original paper of Park and Hofmann should be consulted.

A process of manufacture of the ketones from the secondary alcohols by catalytic dehydrogenation over a brass catalyst at 500° to 800° C. has been described by R. R. Williams and D. H. White,[87] and by catalytic oxidation by A. A. Wells.[88]

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Petroleum and Petroleum Gases *as* Chemical Raw Materials

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PETROLEUM, natural gas and olefine containing refinery gas may all be looked upon as chemical raw materials of great importance. The study of the chemistry of the aliphatic hydrocarbons occurring in petrol fractions is far from complete. Valuable information is being acquired, however, on constituents of the lower-boiling fractions obtained from certain crude oils.

Natural gas is discussed as a potential source of hydrogen, carbon monoxide—hydrogen mixtures (and hence methanol and higher alcohols), formaldehyde and acetylene. The dehydrogenation of paraffin gases to olefine gases is of importance in their possible utilization. The pyrolysis of paraffin and olefine gases gives appreciable yields of aromatic liquids of which about half is benzene.

Refinery gases from vapor-phase oil-cracking processes can supply large quantities of olefine gases, and smaller quantities of diolefines. The syntheses of alcohols, esters and other organic chemicals, valuable in synthetic processes or as solvents, plasticisers, etc., are discussed. The formation of synthetic lubricating oils and the production of resins by polymerization of olefines are interesting recent developments.

Recent work on the separation of pure hydrocarbons from crude oil is described. In the separations elaborate fractionation methods were used.

The identification of the sulphur compounds present in petroleum distillates arouses interest as regards their utilization in the preparation of thioethers, sulphonium compounds, sulphonates, sulphonal, etc.

Some minor constituents of petroleum distillates such as nitrogenous bases, phenols and naphthenic acids are briefly described.

Oxidation may become important in the chemical utilization of petroleum and petroleum gases, but the difficulties of controlling reactions of this type are appreciable. Aromatic hydrocarbons are readily oxidized by air in the vapor-phase in the presence of vanadium pentoxide. Recent work suggests that pressure-oxidation of aliphatic hydrocarbons in the presence of a limited supply of air is a process worth further investigation.

The paper is presented not as an exhaustive account of the potentialities of petroleum and petroleum gases as chemical raw materials, but is intended to indicate several directions in which development may take place.

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PETROLEUM in the past was looked upon solely as a source of liquid fuels, burning oils, lubricating oils and a few other commodities such as wax and pitch. Today every effort is being exerted to make the fullest use of petroleum and its products, and remunerative directions of development include the production of liquefied gases, gas black, solvents, insecticides, cosmetic and medicinal preparations, oils employed in various food industries, water-proofing preparations, emulsifying agents, special cokes and chemical intermediates. At the present moment the production of chemical intermediates cannot be said to figure at all largely in the development of the uses of petroleum and its products, but they are of great importance and are progressively increasing in extent of production. Probably the only chemicals prepared today in any quantity from petroleum and its products, apart from the petroleum gases such as propane, *iso*butane, and butane, are pentane and hexane from light naphthas, mainly derived from natural gas, and the alcohols:—*iso*propyl, secondary butyl, secondary amyl and secondary hexyl, from refinery gases. Further chemicals are derived from pentane and *iso*pentane, through chlorination, including chloro-compounds, amylenes, primary, secondary and tertiary amyl alcohols.

Natural gas and the olefine-containing refinery gases constitute ready sources of chemical products.

The development of the production of chemicals from natural gas is thus comparatively simple, but the utilization of the liquid constituents of petroleum is hampered by two main causes, namely, the complexity of and wide variation in the composition of crude oils and the deficiency in the present state of knowledge of aliphatic hydrocarbons as regards their chemical and physical properties.

In the past, the paraffin series of hydrocarbons was only described in a very general manner. Today the paraffin series may be differentiated as regards straight and branched chain members. Members of compact molecular structure show good anti-knock value as fuels in the internal-combustion engine while straight-chain members are poor in this property. The experiments recently carried out on the oxidation characteristics show that, as regards temperature coefficient of gaseous reaction, those hydrocarbon vapors which have low

values are usually of anti-knock properties. The latter contributions to the kinetics of the gaseous oxidation reactions are of importance in consideration of possible synthetic processes.

The application of thermodynamics to reactions of petroleum derivatives and the simpler aliphatic and aromatic substances has been well investigated, and results have been published on the calculation of the free energies of a number of such organic substances. In this way the whole subject of possible syntheses of organic compounds from petroleum products is being approached upon a sound practical and theoretical basis.

Much of the earlier work on the isolation of pure hydrocarbons from petroleum and its distillates is of questionable value. The experimental difficulties were possibly not appreciated in those days and possibly the equipment was not so readily available. For the isolation of pure constituents, a large quantity of a very narrow cut, such as can be prepared in a bubble tower, is much to be preferred as a starting material than laboratory fractions of usually wider boiling range.

It is common experience to find appreciable divergence in the physical constants of many aliphatic hydrocarbons recorded in the literature by different investigators for the same chemical entity.

For use as standards in aliphatic hydrocarbon research, some pure hydrocarbons can be obtained readily from vegetable sources, *e.g.* *n*-heptane from Pinus Sabiniana oil. These and synthetic hydrocarbons provide the necessary standards when investigating hydrocarbon components of petroleum.

The complexity of aliphatic hydrocarbon chemistry as regards isomerism should encourage rather than deter investigators in this field. Every investigation contributing one or more facts to this branch of chemistry is of great value. Though the field of aliphatic chemistry has been well explored, it is of interest that the two important reactions, namely the cracking of methane to form aromatic hydrocarbons and the reduction of carbon monoxide to methanol and higher alcohols, escaped notice until fairly recent times.

The following account is presented not as an exhaustive account of the potentialities of petroleum and petroleum gases as chemical raw material, but as an indication of several directions in which development may take place.

A general survey of the present relation of the petroleum industry to sixteen other chemical industries has been recently given.[1]

NATURAL GAS AND ITS POSSIBLE UTILIZATION

The utilization of natural gas for the production of chemical products has been reviewed recently by Stanley,[2] Smith[3] and by Frolich and Wiezevich.[4] The enormous quantity of natural gas produced with oil, especially in the early days of the development of an oil field, is well known, and despite the progressive tendency towards conservation, large quantities have been burned to waste.

The chief contituents of natural gas are the lower paraffin hydrocarbons. Gases containing considerable amounts of higher paraffin hydrocarbons up to octane, as the result of association with petroleum, are known as "wet" gases, and those consisting chiefly of methane as "dry" gases. Besides the gaseous paraffin hydrocarbons, other gases may be present, such as carbon dioxide, hydrogen sulphide, and occassionally nitrogen and helium. It is probable that naphthene and benzene vapors are present in some natural gases.

The following analysis of a natural gas from a well in Fremont County, Wyoming, U.S.A., can be considered typical:—methane, 81.30 per cent; ethane, 8.94 per cent; propane, 4.90 per cent; butane, 1.66 per cent; pentane, 0.60 per cent; hydrogen sulphide, nil; carbon dioxide, trace; nitrogen, 2.60 per cent.

In the following table the variation in composition of some natural gases is shown:

Country	Methane, %.	Ethane and Higher Paraffins, %	Nitrogen, %	Carbon Dioxide, %	Hydrogen Sulphide, %	Helium, %
U. S. A.						
Pittsburg, Pa. (City gas)	84.7	13.7	1.6	.....	.....	.....
Los Angeles, California	77.5	16.0	.....	6.5	.....	.....
McKittrick, California	66.2	1.0	2.4	30.4	.....	.....
Fort Smith, Ark	99.2	.....	0.6	0.2	.....	.....
Glasgow, Ky	23.6	69.7	3.8	.....	2.9	.....
Dexter, Kan	14.9	0.4	82.7	.....	.....	1.84
CANADA						
Medicine Hat, Alberta	90.0	3.0	5.0	0.8	.....	.....
Turner Valley, Alberta	71.8	25.9	6.9	2.1	.....	.....
PERSIA						
High Pressure Gas	81.0	16.0	1.4	0.7	0.9	.....
Low Pressure Gas	36.0	52.6	1.7	1.9	7.8	.....

In the light of recent activity in the mineral oil hydrogenation process, and in the synthesis of methanol, the formation of hydrogen and carbon dioxide by the interaction of natural gas and steam in the presence of catalysts is of importance. Methane also reacts with steam, in the presence of catalysts, at 900°C. to form a mixture of carbon monoxide and hydrogen. Such a mixture of carbon monoxide and hydrogen is the starting material in several syntheses.

Reaction Products from Carbon Monoxide and Hydrogen

Carbon Monoxide and Hydrogen

By interaction in the presence of various catalysts which are, in many cases, specific for the product required.

At Atmospheric Pressure.	At Moderate Pressure.	At High Pressure.	At High Pressure.
Saturated and unsaturated aliphatic hydrocarbons, with small amounts of oxygenated compounds (Fischer and Tropsch Elvins and Nash).	Paraffin hydrocarbons solid and non-volatile (Fischer and Tropsch).	Mixture of alcohols and other oxygenated compounds (B.A.S.F. "Synthol" of Fischer).	Pure Methanol (B.A.S.F. Patart Audibert).

Of the processes given in the above table, the production of methyl alcohol is the only one that has attained large-scale working.

Formaldehyde, a product of oxidation of methane, is of great importance as a chemical intermediate.

The conversion of paraffin hydrocarbons into olefines

by dehydrogenation under the influence of heat or partial oxidation is an important step in the preparation of many chemical materials. According to the free energy calculations of Francis,[5] the direct removal of hydrogen from a paraffin to form an olefine with the same number of carbon atoms is possible only at high temperatures and to a limited extent.

It has been reported[6] that a process for the conversion of ethane to ethylene has been carried out commercially. The figures obtained in the static cracking experiments of Williams-Gardner[7] upon ethane show the amounts of products formed:

Gaseous Products from Ethane Heated at 700°C.

	Duration of heating, minutes			
	1.	15.	30.	60.
Hydrogen, %	6.83	8.13	20.83	26.3
Acetylene, %	0.49	0.96	0.62	0.29
Higher Olefines, %	0.93	2.04	2.19	2.21
Methane, %	7.59	35.69	48.89	59.2
Ethylene, %	5.21	13.42	10.26	8.94
Unchanged Ethane, %	78.86	29.99	18.59	8.8

Pease and Durgan[8] have studied the reversible reaction: $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ and obtained equilibrium data at 600°, 650° and 700°C. The equilibrium was approached from both sides, and, apart from some uncertainty due to the simultaneous formation of methane, there were indications that the equilibrium constants at the three temperatures were 0.031, 0.082 and 0.20 respectively.

Similar dehydrogenation reactions take place on heating propane and the butanes, but as the series is ascended there is an increased tendency for a paraffin to be split off to give a lower olefine, thus:

$$\text{Propane} \begin{cases} \nearrow \text{ethylene} + \text{methane} \\ \searrow \text{propylene} + \text{hydrogen.} \end{cases}$$

In the cracking of *n*-butane the major products are propylene and ethylene, while *iso*butane gives chiefly *iso*butylene and propylene.

The separation of olefines and paraffins boiling near each other has been the subject of a certain amount of work; for example, it is claimed that a ready separation of such hydrocarbons as butane and butylene is effected by fractional distillation under suitable pressure in the presence of liquid anhydrous ammonia or methylamine. Other methods[9] of separation depend on the solubility of gaseous olefines in ammoniacal solutions of cuprous and other salts.

Perhaps the most promising method of producing olefines from paraffin hydrocarbons is by partial oxidation at elevated temperatures. Pease[10] has shown that a good yield of olefines may be obtained by oxidation of butane with air at relatively high temperatures.

THE PYROLYSIS OF HYDROCARBON GASES

The pyrolysis of natural gas and refinery gas at high temperatures, to form aromatic liquids, of which about half is a spirit chiefly consisting of benzene, has been discussed by the authors in a previous paper.[11] The pyrolysis of paraffin and olefine hydrocarbons has been investigated recently in some detail and the following table gives the yields of aromatic liquids obtained.

Pyrolysis of Paraffin and Olefine Hydrocarbons for the Production of Aromatics at Atmospheric Pressure
(Dunstan, Hague and Wheeler)

Gas	Temp. °C.	Conversion to Liquids %	Conversion to Spirit. %	Approx. Gals. per 1000 Cu. Ft. Oils	Approx. Gals. per 1000 Cu. Ft. Spirit
Methane	1,050	8.8	5.0	.....	.....
Ethane	850	17.93	11.2	1.7	1.1
	900	21.9	10.63	2.1	1.0
Propane	850	23.09	11.65	3.25	1.6
Butane	800	20.4	12.91	4.0	2.4
	850	24.55	11.64	4.6	2.35
Pentane	850	26.8	11.87	.....	.....
Hexane	800	33.7	19.2	.....	.....
	850	33.8	19.0	.....	.....
Ethylene	800	36.1	17.7	.....	.....
Propylene	750	35.6	20.4	.....	.....
	800	40.6	19.0	.....	.....
$\Delta\alpha$-Butylene	700	35.8	23.6	.....	.....
$\Delta\beta$-Butylene	750	39.6	22.45	.....	.....
	700	37.0	25.8	.....	.....
	750	39.6	23.2	.....	.....

Several recent publications describe the pyrolysis of hydrocarbons.[12]

The cracking of natural gas at temperatures about 800°C. to form aromatic hydrocarbons including benzene, has accordingly been suggested. The Anglo-Persian Oil Company have carried out some semi-large-scale tests using two types of gas, of the following composition:

Constituent	Gas No. 1	Gas No. 2
Hydrogen Sulphide, %	0.9	7.8
Oxygen and Carbon Dioxide, %	0.7	1.9
Nitrogen, %	1.4	1.7
Methane, %	81.0	36.0
Ethane, %	16.0	32.0
Propane, %	.....	9.0
Butane, %	.....	9.0
Pentane, %	.....	6.0

On pyrolysis, gas No. 1 gave about 220 gallons of benzole per 1,000,000 cubic feet, while gas No. 2 gave 770 gallons for the same amount of gas, besides quantities of tar. It is evident that gases comparatively rich in hydrocarbons higher than methane, give better yields of benzole than gases consisting chiefly of methane.

In the treatment of methane at very high temperatures, such as by spark discharge,[13] acetylene is formed. Acetylene is of value as regards its hydration reaction to acetaldehyde, which is the starting material for acetic acid, acetic anhydride and acetone. Acetylene also reacts with acetic acid to produce ethylidene diacetate, which can be decomposed by heat, in the presence of a catalyst, to form acetic anhydride and acetaldehyde. Acetals have been prepared by the interaction of acetylene with alcohols in the presence of mercury catalysts. Acetone has recently been suggested as a starting material for the formation of di-*iso*butylene at high pressures.[14] Recently a chart has been compiled by Lowy on the products derived from acetylene which includes: chloroprene, vinylacetylene, divinylacetylene, acetylene black,

quinaldine, dimethyl-dihydroanthracene, vinyl acetate, ethylidene ether of glycol, crotonaldehyde, *n*-butanol, pyrazole, di-iodoacetylene, synthetic drying oil, etc. Partial combustion[15] of methane to produce acetylene has also been investigated.

REFINERY AND OTHER OLEFINE-CONTAINING GASES

The gases produced in the cracking of oil contain considerable quantities of olefines, those derived from vapor-phase processes being richer than liquid-phase cracking gases. The following table shows typical analyses of liquid- and vapor-phase cracking gases:

Analysis of Gases from Cracking Processes

	Liquid-phase Cracking Process (Cross)	Vapor-phase Cracking Process (Gyro).
Methane and Hydrogen, %	46.3	35.4
Ethylene, %	1.23	22.9
Ethane, %	16.6	13.3
Propylene, %	5.3	18.1
Propane, %	16.2	0.0
Butenes and Butadiene, %	4.3	5.5
Butanes, %	6.1	1.4
Pentanes and heavier, %	3.7	3.4

The proportion of the various olefines in the olefine fraction of a cracking gas varies with the cracking stock and the process conditions. However, the following is a typical analysis of the olefine fraction of a gas which represented 55.75 per cent of a vapor-phase cracking gas:

Analysis of Olefines from Cracking Gas
(Dunstan)

	%
Ethylene	54.0
Propylene	28.0
Butylene	9.0
Amylene	1.7
Higher Olefines	6.1
Butadiene	1.2

It has been stated by Wagner[16] that in a modern Gyro plant a throughput of 4000 barrels of gas oil results in the production of nearly 5,000,000 cubic feet of gas containing olefines to the extent of about 1,350,000 cubic feet of ethylene, 800,000 cubic feet of propylene, and 450,000 cubic feet of the three butylenes.

Large quantities of olefines are present in the gases produced by the high-temperature cracking of oil for carburetting water gas and for the production of Pintsch and Blau gases. Analyses of gases manufactured from oil by high-temperature cracking have been given by Kewley.[17] In the Pintsch process the yield of gas is approximately 74 to 80 cubic feet per gallon of oil used, or about 13 gallons of oil per 1000 cubic feet of gas, the latter containing 36 per cent of unsaturated hydrocarbons. Similar high contents of unsaturated hydrocarbons are formed in the Mansfield process, but the oil-gas manufacturing processes employing partial combustion appear to yield gases of considerably less unsaturated content.

The manufacture of Blau gas entails the production of a special form of Pintsch gas and its separation into two portions of different density. Mineral seal or solar oil is cracked at 600-700° C., and after purification the gaseous products are compressed to 100 atm. The ethane, butane, *iso*butane, etc., are liquefied, and under the existing pressure conditions almost all the ethylene and some of the methane present are dissolved in the liquefied gases. The undissolved gases are removed and the liquid, called Blau gas, is stored in steel cylinders. On release, the liquid evaporates completely giving a gas of the approximate composition: paraffin hydrocarbons 39 per cent (by volume), aromatic and unsaturated hydrocarbons 61 per cent. The latter fraction is made up of ethylene (18.5 per cent), butylene (4.5 per cent), acetylene (4.5 per cent), benzene (0.5 per cent), and higher hydrocarbons (33.0 per cent).

The examination, by Birch and Scott,[18] of the lower fractions of comparatively close boiling range, derived from the compression gasoline from a high-temperature cracking unit, and the corresponding gasoline itself (yellow naphtha), showed that butadiene, piperylene, isoprene, and *cyclo*pentadiene were all present, and that these could be separated as their addition compounds with maleic anhydride.

The dibutyl ester[19] of Δ^4-*cyclo*hexene dicarboxylic acid, derived from butadiene and maleic acid, has been patented as a plasticiser for cellulose esters.

Diolefines[20] are stated to be absorbed by cuprous chloride in neutral solution containing an alkali or alkaline-earth chloride and a small quantity of a reducing agent, *e.g.* hydroxylamine hydrochloride and stannous chloride.

CONVERSION OF OLEFINES TO ALCOHOLS AND OTHER CHEMICAL SUBSTANCES

The olefine mixtures can be separated by pressure and by treatment with different strengths of sulphuric acid. Generally, the olefines may be converted into alcohols by the following methods: direct hydration either in the liquid or gaseous phase under the influence of catalysts, esterification of olefines by means of sulphuric or sulphonic acids followed by the hydrolysis of the ester formed, esterification of the olefine by means of hydrogen halides or organic acids followed by hydrolysis. The direct hydration processes are commanding much attention today. On thermodynamic grounds it should be possible to synthesize alcohols from the corresponding olefines by reaction with steam in the vapor-phase under suitable conditions. The yields of alcohols obtained in this way are usually very small, and side reactions such as polymerizations are generally the disturbing influences. Sulphuric acid and silver sulphate on pumice, and certain other catalysts such as phosphates, have recently been patented[21] as catalysts in this reaction. So far, only the method involving the sulphuric acid absorption of olefines is generally applied.

At the moment, very little ethyl alcohol is made from

petroleum gases, but a great potential supply of ethylene exists for utilization in this way when economically possible.

There are many points of interest in these alcohol syntheses. The apparently simple problem of the conversion of ethylene to alcohol, by absorption in sulphuric acid and hydrolysis of ethyl sulphuric acid or diethyl sulphate, is a reaction which needs very careful control. Under certain conditions hydrocarbons can be formed by the polymerization of ethylene. Too strong an acid can convert ethylene to carbyl sulphate which will not hydrolyze to ethyl alcohol. Many investigators have studied the effect of varying the conditions of the absorption of ethylene in sulphuric acid, without catalysts. Damiens has examined the effect of the following factors on the absorption of ethylene, such as: composition of the acid, efficient gas-acid contact, partial pressure of ethylene, temperature of absorption, and the presence of catalysts in the acid. Sulphuric acid of 99.5 per cent strength was found to give an absorption velocity of three to five times that of a 95.5 per cent acid. Cuprous compounds were found to be good catalysts. Other investigators have found silver sulphate to be a good catalyst, and a recent patent recommends the use of ferri- and ferro-cyanides which are claimed to suppress oily product formation. However, most catalysts suffer from the objection that they become deactivated eventually by tarry deposits, and should be avoided if possible.

The alcohols produced from cracking gases are *iso*propyl alcohol, secondary and tertiary butyl alcohols, and secondary amyl alcohol, and of these *iso*propyl alcohol is the most important; secondary hexyl, heptyl, and octyl alcohols could also readily be prepared.

Ethyl alcohol, and secondary alcohols from *iso*propyl to secondary hexyl, are prepared by absorption of the olefine in sulphuric acid, the alcohols being recovered by hydrolysis of the alkyl sulphuric ester and subsequent rectification.

Ethyl and *iso*propyl ethers are formed together with the alcohols. Ethers of ethylene glycol are prepared by treating an alcohol with ethylene oxide. Ketones such as acetone and methyl ethyl ketone are made by dehydrogenating the secondary alcohol. Partial oxidation in the presence of catalysts is a promising method for converting secondary alcohols to ketones. The esters of the alcohols previously discussed are obtained by the reaction of a fatty acid and an alcohol in liquid or vapor phase with suitable catalysts, or by treatment of the alkyl sulphuric ester with the calcium salt of a fatty acid. *iso*Propyl acetate is commercially prepared by this process. *iso*Propyl alcohol can also be used as a starting material for preparing such compounds as propyl chloride, chloroacetone, acetone, etc.

The production of xanthates has recently been patented.[22] Alkali metal *sec-* or *tert-* alkoxides treated with carbon disulphide give xanthates, which are suggested as flotation agents, insecticides, or vulcanization accelerators.

The chief chemical intermediate obtained from ethylene is the chlorohydrin from which ethylene oxide and ethylene glycol can readily be prepared. The use of ethylene glycol in explosives and anti-freeze agents is well known. Ethylene chlorohydrin vapor has been found to break the dormancy of sugar maple and chestnut seedlings.

Many solvents, especially for lacquers, are now prepared from ethylene glycol. The following are examples. Ethylene glycol monoethyl ether, "Cellosolve," is a good solvent for cellulose nitrate but not for cellulose acetate. It has but little odor, is miscible with water and dissolves ester gums, glyceryl phthalate, resin, etc. Ethylene glycol monoethyl ether monoacetate is a useful derivative. Ethylene glycol monomethyl ether is a solvent for cellulose acetate and nitrate, shellac, kauri and colophony. Diethylene glycol monoethyl ether, "Carbitol," is a solvent for shellac, cellulose nitrate and colophony, and is used in textile soaps and in the dye industry. Dioxane (diethylene dioxide) is also a solvent for ester gums, glyceryl phthalate, vinyl resins, shellac, and cellulose acetate. Triethanolamine is a viscous hygroscopic liquid boiling at 277° C. under 150 mm. pressure. It is soluble in most organic liquids containing combined oxygen, but is only slightly soluble in hydrocarbons. It is mildly alkaline and its dissociation constant is 2.5×10^{-6}. Its fatty acid soaps, such as the oleate, are valuable emulsifying agents. These viscous soaps are soluble in practically all organic liquids including hydrocarbons. These soaps are valuable for the following purposes: mineral oil emulsions for textile lubricants, machine-cutting oils, wax emulsions, cosmetic creams, emulsions of solvents for polishes, disinfectants, kerosene emulsions for sprays, and dry cleaning detergents. The use of ethanolamine bases for the continuous removal of carbondioxide and hydrogen sulphide from gases has recently been indicated.

The separation of carbon dioxide from hydrogen by scrubbing under pressure with triethanolamine is a feature of the Baton Rouge petroleum-hydrogenation plant.[23]

The suggested use of $\beta\beta'$-dichloroethyl ether[24] ("Chlorex") as a selective solvent in the refining of lubricating oils is of interest. Again, the possible use of certain chemical substances,[25] including dichloroethyl ether, to increase the load-carrying power of extreme-pressure lubricants, is an application of these substances worthy of more research.

Many interesting facts about the application of pure hydrocarbon gases and synthetic organic chemicals which could be obtained from natural gas and petroleum products have been described recently by a large chemical organization.[26]

OTHER MEANS OF UTILIZATION OF OLEFINES

The plymerization of olefine hydrocarbons can be effected by the following influences: Ultra-violet light, silent electric discharge, heat, pressure, and catalysts.

Ethylene is polymerized by heat to butylene which on further heating is considered to be dehydrogenated to butadiene, which can then condense with more ethylene to form *cyclo*hexene. The latter at higher temperatures would readily be converted to benzene. Benzene formation from olefines has been mentioned earlier in this paper. Collie was one of the earliest workers on the effect of the silent electric discharge on these substances and obtained liquid hydrocarbons from ethylene.

This principle is the basis of the Electrion oils and Voltols, which are mineral and fatty lubricating oils increased in viscosity by such treatment.[27] By the action of the silent electric discharge, hydrogen is considered to be split off oil molecules and the residues to combine to form more complex substances.

The effect of catalysts and increased pressure on the polymerization of olefines presents a fruitful field for research. Aluminum chloride and boron trifluoride are important catalysts for causing olefine polymerization. With aluminum chloride, there is every reason to believe that reactions of the Friedel-Craft type occur, as it is known that unsaturated hydrocarbons such as ethylene can undergo this reaction with other substances to produce alkylated aromatic hydrocarbons, alkyl vinyl ketones, halogenated acid chlorides, etc. The synthetic lubricating oils, produced from ethylene and other olefines by the action of aluminum chloride, have been described by the authors,[28] and by Sullivan, Voorhees, Neeley and Shankland.[29] These oils show some remarkable similarities to natural petroleum lubricating oils yet differ in many ways from them.

Many patents cover the formation of synthetic lubricating oils by the condensation of olefines with aromatic hydrocarbons in the presence of aluminum chloride.

An interesting development for the utilization of ethylene has been discussed recently by Nugey,[30] namely, its use in the production of the new plastic resin, metastyrene. The paper includes a description of the design and erection of a plant for the extraction of ethylene from cracking gases. Synthetic resins produced by the action of anhydrous aluminum chloride on unsaturated petroleum distillates have been described by Thomas and Carmody.[31] The reactions involved are many and complex, and probably include the reaction of olefines to form oily polymers, reaction of olefines with aromatics to form substituted aromatics, polymerization of diolefines and olefines to form resins, and reaction of diolefines with substituted aromatics to form resins.

Recent suggested syntheses from ethylene include its oxidation to glyoxal[32] in the presence of selenium dioxide or selenous acid at 50-350° C.

Ethylene is used to some extent in the fruit industry. In studying the effect of ethylene on the activity of diastase and invertase, Englis and Zannis[33] came to the conclusion that the effect of ethylene in ripening fruit is primarily concerned with a color change rather than a true ripening process.

RECENT WORK ON THE ISOLATION OF HYDROCARBON CONSTITUENTS FROM LIGHT PETROLEUM FRACTIONS

To estimate the potentialities of petroleum as a chemical raw material, a detailed knowledge of the constituents of petroleum fractions is necessary. For the reasons stated previously, very little is yet known of the constituents of even the spirit fractions of crude oils, and unfortunately much of the early work on the isolation of pure hydrocarbons is of little value. There has been, however, a decided move towards the accumulation of accurate information on the hydrocarbon and other constituents of petroleum. Of the many investigators concerned, mention may be made of the work of Carpenter on Burmah oil fractions, Birch and Norris on Persian oil distillates, Tongberg and Fenske on Pennsylvania fractions, and Bruun, Hicks-Bruun, White Rose, Leslie and Schicktanz on Mid-Continent (Oklahoma) crude oil. This list is far from complete, but the work of these investigators will be reviewed and can be taken as indicative of the type of research so urgently required in this field.

Carpenter[34] indicates the presence of benzene, toluene, the xylenes and higher aromatic hydrocarbons in Burmah crude oil fractions. Birch and Norris[35] identified in Persian oil fractions: toluene, *m*-xylene, *p*-xylene, *p*-ethyltoluene, mesitylene, ψ-cumene, hemimellithene, a diethylbenzene, an ethylxylene, naphthalene, and β-methyl-, dimethyl-, and trimethyl-naphthalenes. Tongberg and Fenske[36] isolated from straight-run Pennsylvania gasoline: β-methylpentane, *n*-heptane, methyl*cyclo*hexane, and *n*-octane, and in the course of their work found that *n*-heptane and methyl*cyclo*hexane did not form a constant-boiling mixture and that the constant-boiling mixture of benzene and *n*-hexane was of widely different composition from the accepted value. *n*-Octane has been separated from a fraction of an Oklahoma crude oil by alternate fractional distillations and crystallizations by Leslie and Schicktanz.[37] Isomers of hexane have been isolated from Oklahoma crude oil by Bruun and Hicks-Bruun.[38] Fractional distillation concentrated the hexanes in a series of constant-boiling mixtures containing cyclic compounds. Ethyl alcohol was added to these mixtures, and redistillation yielded constant-boiling mixtures of alcohol and the hexanes; thus were separated: βγ-dimethylbutane, β- and γ-methylpentanes, and *n*-hexane. Toluene has been isolated from Oklahoma crude oil fractions by Bruun, Leslie and Schicktanz.[39] *cyclo*Hexane has also been isolated by Bruun and Hicks-Bruun.[40] By the use of the technique of fractional distillation and subsequent equilibrium melting in a low temperature centrifuge, Bruun and Hicks-Bruun[41] have isolated pure *n*-decane. These investigators[42] have also isolated and determined the percentage of methyl*cyclo*pentane in this Mid-Continent petroleum, and have isolated[43] and determined the proportion of *n*-heptane and of methyl*cyclo*hexane in Oklahoma petroleum. The latter work included a determination of the phase-equilibrium

diagram for the condensed system *n*-heptane and methyl*cyclo*hexane. *n*-Nonane has been isolated by White and Rose,[44] and these two investigators[45] found the *ortho, meta-* and *para*-xylenes to occur in the ratio of 3:3:1 in the same crude oil. Later work by Bruun and Hicks-Bruun[46] has shown the probable presence of $\beta\beta$-dimethylpentane in this Mid-Continent oil.

Such hydrocarbons as those mentioned above may ultimately be separated in quantity for chemical purposes.

ISOLATION AND POSSIBLE APPLICATION OF PURE SULPHUR COMPOUNDS FROM PETROLEUM DISTILLATES AND SPENT REFINING AGENTS

Free sulphur and organic sulphur compounds are present in many crude oils, and on account of their odor or other undesirable properties are removed in the refining of petroleum distillates. Hydrogen sulphide is a constituent of many natural gases and thus of the oils associated with these. At atmospheric pressure, hydrogen sulphide is generally not retained by the oil in any great quantity. The fact that some crude oils containing sulphur are of sweet odor while the distillates are sour shows that some chemical reaction has taken place during the distillation processes. The sulphur-compounds of Persian oil have been investigated by Birch and Norris,[47] who pointed out that distillates contained elementary sulphur, mercaptans and neutral sulphur compounds. From refinery "spent soda," *iso*propyl mercaptan, *iso*butyl mercaptan and two fractions presumed to contain respectively ethyl mercaptan and *iso*amyl mercaptan were isolated. The mercaptans are readily oxidized to disulphides and of the latter Birch and Norris isolated, from the "spent soda," diethyl disulphide, di-*iso*propyl disulphide, and di-*iso*butyl disulphide.

The subject of sulphur compounds derived from petroleum has been discussed by Wiezevich, Turner and Frolich.[48] It is suggested by these authors that the mercaptans can be used as odorants, denaturants and raw materials. The heavier mercaptans form oil-soluble lead salts. Ethyl mercaptan reacts with acetone in the cold and in the presence of anhydrous zinc chloride or hydrogen chloride to produce acetone diethyl mercaptole which, on distillation at atmospheric pressure, decomposes, the main compound formed probably being propylene ethyl thioether. Oxidation of acetone diethyl mercaptole gives sulphonal. The thioethers, the sulphides, can be obtained from mercaptans by the aid of catalysts such as cadmium sulphide—zinc sulphide —aluminum oxide at 350° C. Wiezevich, Turner and Frolich point out that methyl sulphide and ethyl sulphide dissolve cellulose nitrate in the presence of ethyl alcohol, the solutions comparing favorably in various properties, such as viscosity, color, odor and drying behavior, with such solvents for cellulose nitrate as are now in industrial use. They suggest the possible use of the thioethers as rubber solvents. Certain resins, such as *p*-coumarone, abietic acids, petroleum resin, *m*- and *p*-cresol—sulphur chloride resin, and xylenol—sulphur chloride resin are very soluble in thioethers. They suggest also the use of thioethers as solvents for Grignard reactions, and as starting materials in the preparation of sulphonium compounds. The disulphides also possess solvent powers.

Numerous other sulphur compounds may be prepared using mercaptans or sulphide as raw materials; for example, oxidation of ethyl sulphide produces ethyl sulphoxide or diethyl sulphone, the former being suggested as a plasticiser for pyroxylin. Ethyl tetrasulphide is formed when ethyl mercaptan reacts with sulphur chloride in carbon disulphide solution. Ethyl mercaptan, when oxidized with potassium permanganate, forms ethyl sulphonic acid, which is of interest as regards the recent use of sulphonates as wetting agents, detergents and demulsifiers.

A considerable amount of valuable research on sulphur compounds has recently been carried out in the U. S. A.

MINOR CONSTITUENTS OF PETROLEUM

The oxy-compounds occurring in some petroleum fractions have been frequently described. Recently[49] the crude naphthenic acids from Caucasian petroleum have been investigated and the following were shown to be present: the fatty acids, *iso*amylacetic and $\beta\beta$-diethyl propionic acids and the cyclic acids, *cyclo*pentane carboxylic acid (probably) and *cyclo*hexane carboxylic acid. Higher fatty acids and phenols from Boryslaw oil fractions have been investigated by Holzmann and Pilat.[50]

A general discussion on the composition of petroleum by v. Braun includes the view that research on the nature of many compounds containing oxygen, nitrogen and sulphur, which have been isolated from petroleum distillates, has definitely established that these compounds do not occur as such in the crude oil, but are formed from more complex compounds by heating or chemical reaction during distillation or by chemical reaction during the treatment necessary for their isolation.

The nitrogenous bases in certain petroleum fractions have been investigated. Recently, Path, Schulze and King,[51] in research upon the bases in the kerosene distillate of Californian oil, identified 2:3:8-trimethyl quinoline. Before dismissing the subject of the minor constituents of petroleum, mention should be made of the ash[52] which in some instances has yielded vanadium; for example, the flue dust from certain burners using Mexican fuel oil contained vanadium pentoxide 22.09 per cent together with nickel, lead and free sulphuric acid.

OXIDATION OF PETROLEUM HYDROCARBONS

The oxidation of petroleum hydrocarbons from methane to heavy oils and waxes has received considerable attention for many years. Investigations have been carried out from many viewpoints and

include such subjects as the formation of formaldehyde or carbon monoxide-hydrogen mixtures from methane, the dehydrogenation of butane to butylene, the vapor-phase oxidation of petrol hydrocarbons[53] as related to their behavior in the internal-combustion engine, and the oxidation of heavy oils and waxes to produce fatty acids.

One feature of many suggested oxidation processes is the complexity of the products obtained, the complexity increasing as the molecular weight of the hydrocarbon increases. Lewis and Frolich[54] have reported results on the oxidation of propane with oxygen at pressures about 2000 pounds per square inch and at temperatures of 300-350° C. They state that under these conditions more than 40 per cent of the oxygen may be accounted for in the liquid organic oxidation products. The products obtained under such conditions of pressure-oxidation of propane are stated to be: acetaldehyde and acetone 6.0 per cent, methyl alcohol 22 per cent, ethyl alcohol 37 per cent, propyl alcohol 7 per cent, formic acid 1.5 per cent and water 26.5 per cent. Cooper and Wiezevich,[55] in their explosive-limit determinations, state that it should be safe to operate with methane at a pressure of 3000 pounds per square inch and temperatures of 400° C. in the presence of less than 10 per cent of oxygen. In a similar manner, formic, acetic and propionic acids and ketones, aldehydes and alcohols are stated to be formed by oxidation of propane, butane and pentane under pressure with oxygen. The partial oxidation of hydrocarbons catalyzed by oxides or nitrogen has been described by Bibb,[56] in whose work formaldehyde was obtained from propane and other hydrocarbons. The methods and apparatus for oxidation of hydrocarbons has recently been described by Marek,[57] who discusses the vapor-phase oxidation of aromatic hydrocarbons in the presence of vanadium pentoxide. Aliphatic hydrocarbons are sensitive to oxidation. The use of high pressures and lower temperature promotes the yield of alcohols, but in such processes, if conditions are not controlled, there is risk of explosion. Hexoic acid[58] has been synthesized from natural-gas pentane by way of chlorides and nitriles. In discussing some technical applications of aliphatic acids, Challenger[59] points out that adipic acid may be obtained by oxidation of those fractions of petroleum which contain *cyclo*hexane. The vapor-phase oxidations[60] of toluene and naphthalene are well-known reactions. Oxidation conditions for heavy mineral hydrocarbon oils have been given by James,[61] who points out that the hydrocarbons of high molecular weight are oxidized preferentially. Much has been published on the oxidation of paraffin wax. A recent patent[62] suggests hydrogenation of the oil prior to oxidation. In this process, hydrocarbon oils containing paraffin wax are treated with hydrogen at 400-470° C. and under 200 atm. pressure, in the presence of oxides. The product is oxidized at 180° C. at atmospheric pressure in the presence of a catalyst such as a stearate or permanganate, and it is claimed that good yields of fatty acids are formed. The identification of products of oxidation of gas oil by the Penniman process (oxidation of gas oil by air at 399° C. and 300 pounds per square inch pressure) has been carried out by Swann, Howard and Reid.[63] In the aqueous part of the distillate obtained, acetaldehyde, acetone, methyl alcohol, methyl acetate, ethyl alcohol, ethyl acetate, acetic acid, allyl alcohol and dimethyl acetal were found.

CHLORINATION

Chlorination is a very important process in the chemical utilization of petroleum and petroleum gases. Chlorine is a convenient reagent in that it reacts readily with hydrocarbons. The chloro-derivatives are useful substances, a number of them being well known as solvents, and in addition they have very considerable possibilities as starting points for various syntheses.

With reference to the paraffins it is interesting to note that an industry[64] has been built up in America round the chlorination of *n*- and *iso*-pentanes. From a mixture of these hydrocarbons, amyl alcohols and amyl acetates are produced by way of amyl chlorides, which are obtained by chlorinating the hydrocarbon mixture. Other paraffin hydrocarbons do not appear to have been utilized in this way.

The following are the substances produced from the pentanes: *n*-butyl carbinol, *iso*-butyl carbinol, secondary-butyl carbinol, methyl propyl carbinol, diethyl carbinol, secondary amyl alcohols, dimethyl ethyl carbinol, tertiary amyl alcohol, mixed amyl chlorides, *n*-amyl chloride, amylene dichlorides, amylenes, diamylene, amyl ether (diamyl ether), pentasol (a mixture of amyl alcohols), pentacetate (from the acetylation of pentasol with commercial acetic acid).

A considerable amount of work has been done on the chlorination of the paraffins. This has been reviewed by Egloff, Schaad and Lowry,[65] and a brief account of more recent work is given by Nash and Mason.[66]

The reaction between chlorine and the lower paraffins may be brought about photochemically or thermally. In thermal vapor-phase chlorination it is necessary, in order to get the best yields, to adjust the conditions so that though complete or nearly complete reaction is effected, pyrolysis does not occur.[67] Methods of avoiding risk of explosions have been proposed, one being mentioned in a recent patent.[68] Diluents have been used in this connection.

Numerous investigators have studied the chlorination of methane, with very varied experimental conditions. Compared with this, very little quantitative data has been published so far on the homologues from ethane to the butanes.

The results of chlorination processes are complex, for the following reasons. As the hydrocarbon series is ascended the number of possible chloro-compounds increases, in general the intermediate products can undergo further chlorination, and there is a possibility of side reactions such as pyrolysis taking place. It has

been shown that interesting results may be obtained on comparing the results of thermal vapor-phase chlorination reactions, in which catalysts are not used and the conditions are designed to avoid pyrolysis as far as possible, with the theoretical work of Martin and Fuchs.[69] So far comparison has been made in cases of methane, propane and methyl chloride, and toluene and benzene.[70] It is shown that the hydrocarbon: chlorine ratio in the reaction mixture (or percentage of hydrocarbon converted) is very important in determining the results of the reactions.

An interesting example of the use of a chlorinated product in synthesis is furnished by the production of the synthetic oil[71] "Paraflow." Chlorinated Pennsylvanian wax is condensed, in the presence of anhydrous aluminum chloride, with aromatic hydrocarbons such as naphthalene. The viscous hydrocarbon oil of green fluorescence so produced is used to blend in small proportions into paraffin-base lubricating oils to lower their setting point.

There are possibilities also in the conversion of hydrocarbons to other halogen derivatives of value. Methyl bromide[72] is a substance that has been suggested recently for a variety of purposes, including that of a fire extinguisher.

OTHER SUGGESTED PROCESSES AND SYNTHESES IN THE TREATMENT OF PETROLEUM HYDROCARBONS AND THEIR DERIVATIVES

An enormous number of processes have been put forward in the literature and in patent claims for the utilization of petroleum products in a variety of ways. Many of the patent claims require the support of published experimental work before their true value can be assessed. Below is a summary of a number of such processes that have been described recently.[73]

Methane has been suggested as an agent for the reduction of magnetite and limonite, the reduction in the case of limonite occurring at 700° C. The production of hydrogen cyanide by the interaction of gaseous hydrocarbons and ammonia at temperatures of the order of 1350-1450° C. has been patented. For this reaction the surface of the chamber must be of an inactive material, and to prevent decomposition of the reactants, the latter are brought up to the reaction temperature as quickly as possible. Hydrocyanic acid is also shown

(*Continued on page 378*)

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Comparison of . . .

Cracking and Hydrogenation

As Methods of Producing Gasoline

R. T. HASLAM,* R. P. RUSSELL† and W. C. ASBURY†

THE general applicability of the hydrogenation process to the problems of the petroleum industry has been discussed in previous papers.[1,2]. This article deals exclusively with the use of the hydrogenation process for production of gasoline from gas oil.‡ A critical analysis has been made of the factors which affect the economic position of the hydrogenation process, the ability of the process to compete with cracking and its use in conjunction with cracking.

The comparison of hydrogenation and cracking has been made on as broad a basis as possible; the influence of gasoline prices, ranging from the low price now obtaining in the United States to the high price frequently encountered has been studied. The gas oils selected for the comparison include both refractory, low-aniline point, and paraffinic, high-aniline point, stocks met with in normal present-day cracking operations.

Today two general types of hydrogenation are available for the production of gasoline from gas oils; one may be roughly characterized as high-temperature, the other as low-temperature operation. Both types may be carried out in the same apparatus under similar pressure conditions. The former is advantageous where high octane number gasolines are desired, while the latter is especially effective in a range of medium octane number, giving high yields and high conversions.

These two phases of gasoline production by hydrogenation are covered in detail in the following sections.

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Types of Hydrogenation Available for Gasoline Production

A. *High-Temperature Operation.*

As already outlined in earlier articles,[1, 3] the conditions of hydrogenation may be so adjusted that gasolines of high octane number may be produced. Since the temperatures employed in this operation are somewhat higher than generally required in other applications of hydrogenation, this method has been termed "high temperature hydrogenation." In this process, hydrogenation in tensity is so limited that non-paraffinic gasoline is produced, but without the formation of tar or coke. The resulting gasolines are low in sulphur, are gum stable and require only minimum amounts of treating.

This type operation has been demonstrated in the commercial units of the I.G. Farbenindustrie A.G. on a wide variety of gas oils from coal tars and crude oils and in the Pilot Plant of the Standard Oil Company of Louisiana on numerous cracked and virgin gas oils. High-flash high octane number safety fuel and high-solvency paint and lacquer naphthas are among the products made in this operation.

Catalysts available for this type of hydrogenation have shown excellent strength, ruggedness and long life. Recent work in this field has been directed toward the development of more active catalysts. Gratifying progress has been made in improving the physical form in which the catalyst is used and in the discovery of new types.

TABLE I

Comparison of Three Catalysts in the Production of Gasoline at High Temperature from the Same Gas Oil at Periods of Equal Catalyst Age.

SOURCE	Naphtha Bottoms from Mixed Base Crudes		
Feed Stock:			
A. P. I. Gravity	32.3°		
Aniline Point, °F	108		
% Sulphur	0.414		
I. B. P., °F	402		
10% at °F	423		
20% at °F	430		
50% at °F	449		
90% at °F	512		
F. B. P., °F	624		
CATALYST	**A.**	**B.**	**C.**
Operating Conditions:			
Throughput, vol./vol./hr.*	2.0	4.0	4.0
Vol.% Fresh Feed	45	50	58
Vol.% Yield Distillate on Fresh Feed	86	89	90
Volumes Gasoline/Vol. Catalyst/Hour	0.78	1.78	2.09
Inspection of Distillate:†			
A. P. I.	45.0	42.7	45.7
I. B. P., °F	—	102	95
% at 158°F	—	8.0	10.0
% at 212°F	—	19.5	21.0
% at 284°F	—	35.5	36.0
% at 374°F	—	64.0	64.0
F. B. P., °F	420	425	419
% Recovery	—	96.3	97.0
Color, Saybolt	+10	+11	+4
% Sulphur	0.05	0.036	0.02
Glass Dish Gum, mg./100 c.c.	7.0	1.7	1.6
Doctor‡	Negative	Negative	Negative
Corrosion‡	Pass	Pass	Pass
Octane No. at 212°F§	85	82	72

* Volumes of total throughput per volume of catalyst space per hour.
† Distillate as received from hydrogenation unit with no treatment.
‡ After soda wash.
§ Series 30 Engine at 212° F. jacket, 600 R.P.M., and 200 lbs./sq. in. compression.

Typical results of high-temperature hydrogenation obtained with three characteristic catalysts are presented

* Standard Oil Development Company, New York City.
† Hydro Engineering and Chemical Company, Elizabeth, N. J.
‡ This process is based on the fundamental work of the I.G. Farbenindustrie A.G.

in Table I. Catalysts A and B are similar in composition, but the latter has been prepared in a form which exposes considerably more surface than the former. Catalyst C is of the active diluted type developed by the Hydrogenation Laboratories of the I.G. Farbenindustrie and the Shell Company. It will be noted from the table that the more active catalysts B and C are primarily effective in increasing throughputs and conversions. The gasoline production per unit volume of catalyst has been more than doubled by the use of these two materials. These results are of considerable economic importance since they make possible more efficient utilization of high-pressure reaction equipment.

The gasolines produced by these catalysts (Table I) are characterized by their low sulphur and gum contents. They are consistently easier to treat than cracked gasolines from the same stocks. Higher end point gasolines made by high-temperature hydrogenation are more difficult to treat than low end point gasolines, as is the case with cracked naphthas. The type C catalyst, by virtue of its pronounced hydrogenation activity at high temperatures, tends to produce gasolines of somewhat lower octane number than the other two types.

B. *Low-Temperature Operation.*

Catalysts have been available for some years for the low-temperature hydrogenation of gas oils to gasoline. This mode of operation has gained considerably in attractiveness recently by the demonstration of results from a highly active catalyst by the I.G. Farbenindustrie A.G. This company has shown the effectiveness of this material by trial in a number of its commercial hydrogenation units during the past few years on gas oils from crudes and coal tars.

TABLE II
Production of Gasoline from Three Gas Oils by Hydrogenation at Low Temperatures

SOURCE	Lake Venezuela Gas Oil	Cracked Coastal Gas Oil	*Hydrogenated Gas Oil from German Crude
Feed Stock:			
A. P. I. Gravity	25.1	21.5	32.1
Aniline Point, °F	106	50	117
%Sulphur	0.864	—	0.25
I. B. P., °F	360	404	336
10% at °F	470	446	410
20% at °F	491	452	440
50% at °F	536	471	505
90% at °F	652	507	608
F. B. P., °F	684	565	656
Operating Conditions:			
Throughput, vol./vol./hr.†	2.2	2.2	2.6
Vol.% Fresh Feed	64	62	51
Vol.% Yield Distillate on Fresh Feed	109.5	110.6	113.0
Volumes Gasoline/Vol. Catalyst/Hour	1.54	1.51	1.50
Inspection of Distillate:‡			
A. P. I. Gravity	65.0	62.3	69.0
I. B. P., °F	87	85	73
% at 140°F. (see text)	16.5	18.0	10.0
% at 158°F	23.5	23.0	17.0
% at 212°F	43.0	43.0	40.2
% at 284°F	68.0	67.0	69.2
% at 374°F	91.0	90.0	91.4
F. B. P., °F	410	406	390
% Recovery	96.5	95.0	94.0
Color, Saybolt	+28	+30	—
% Sulphur	0.014	—	—
Glass Dish Gum, mg./100 c.c.	1.8	0.0	—
Cu Dish Gum, mg./100 c.c.	5.2	4.8	—
Doctor	Pass	Pass	—
Corrosion	Pass	Pass	—
Octane No. 212°F §	63.5	66.8	61.0

* Data of the I.G. Farbenindustrie.
† Volumes of total throughput per volume of catalyst space per hour.
‡ Distillate as received from unit and washed with caustic.
§ Series 30 Engine at 212° F. jacket, 600 R.P.M. and 200 lbs./sq. in. compression.

TABLE III
Octane Number Fade of Low-Temperature Hydrogenation Gasoline

Gasoline Hydrogenated Lake Venezuela Gas Oil:	
A. P. I. Gravity	66.8
% at 212°F	47.0
90% Point	334°F
Final Boiling Point	377°F
Color (Saybolt)	30
Octane Numbers on Series 30 Motor:	
(*a*) At 212° F. Jacket, 190-200lb/sq. in., 600 R. P. M.	
Above Gasoline without Lead per U. S. Gal.	66.0
With 1 c.cm. Lead Tetraethyl " " ...	76.6
" " " " " ...	82.5
(*b*) At 300° F. Jacket, 200lb/sq. in., 600 R. P. M.	
Above Gasoline without Lead	62.5
With 1 c.cm. Lead Tetraethyl per U. S. Gal.	75.6
" 2 " " " "	79.7
(*c*) At 375° F. Jacket, 200-220lb/sq. in., 900 R.P.M.*	
Above Gasoline without Lead	61.5
With 1 c.cm. Lead Tetraethyl per U. S. Gal.	75.1
Octane Numbers on the C. F. R. Engine:	
C. F. R. Motor Method (212°F., 900 R. P. M.*)	
Above Gasoline without Lead	66.1
With 0.5 c.cm. Lead Tetraethyl per U. S. Gal.	73.1
With 1.0 " " " " "	77.9
" 2.0 " " " " "	80.6

* This method now the A.S.T.M. Standard procedure.

The outstanding characteristics of the performance of this catalyst are:

(*a*) High yields—on the average up to 110 gallons of gasoline are produced from every 100 gallons of gas oil.

(*b*) High conversions per pass—usually 50 to 100 per cent better than that possible on catalysts previously used.

(*c*) The gasoline produced is of high volatility (40-45 per cent off at 212° F.) and requires no finishing treatment other than a caustic or soda wash, followed by a light doctor sweetening.

Table II presents operating results obtained on three low aniline point gas oils with this catalyst. It will be noted that, even on these refractory stocks, the yields ranged from 109.5 to 113 per cent on the feed, the gasoline throughput per unit volume of catalyst is excellent, and the gasolines are of low gum, low sulphur and high volatility. These gasolines contain a large amount of light ends (note per cent to 140° F. in Table II). Provided the situation permitted, the refiner would normally blend off the hydrogenated gasoline with gasolines deficient in light ends. If, in a given refinery, sufficient gasoline, deficient in lighter boiling constituents, were not available, it would be necessary to eliminate these light ends to meet volatility specifications. This would reduce the actual gasoline yields of the hydrogenation operation to 102 to 106 per cent. As a specific example, a low-temperature hydro gasoline of 383° F. end point, 21.8 per cent distillation plus loss at 140° F. and 46.5 per cent at 212, after removal of 1.5 per cent propane and 5 per cent butane by fractionation

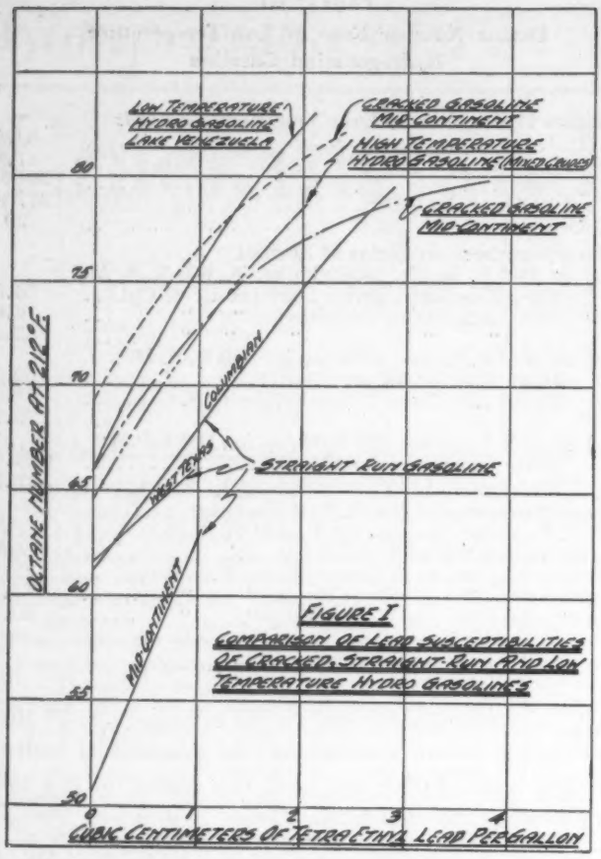


FIGURE I

COMPARISON OF LEAD SUSCEPTIBILITIES OF CRACKED, STRAIGHT-RUN AND LOW TEMPERATURE HYDRO GASOLINES

showed a 9.6 pound Reid vapor pressure (equivalent to about 12.5 per cent distillation plus loss at 140° F.). When cutting higher end point gasoline smaller reduction in yield would be required to meet volatility specifications. Recent investigations indicate that the operating conditions may be changed to reduce the per cent off at 140° without loss in total yield. Although the gasolines made by this method are of medium octane numbers, they have the advantage of losing only a few points in octane number at high engine jacket temperatures. This resistance to "fading" at high jacket temperature is shown by the following knock-test data [Table II and III] obtained on a gasoline made by low-temperature hydrogenation.

Cracked gasolines of similar octane number at 212° F. and similar volatility usually lose 8-12 octane numbers over the jacket temperature range 212° to 375° F. It should be borne in mind, however, that the average cracked gasolines are normally of higher octane number than that shown in Table III. The gasolines made by low-temperature hydrogenation are very susceptible to additions of lead tetraethyl. A comparison of the lead susceptibility characteristics of straight-run, cracked, and hydro gasolines is given in Figure 1. The low-temperature hydro gasoline is superior to cracked gasolines and better than most straight-run gasolines of similar volatility. Reference to Table III shows that lead-treated low-temperature hydro gasoline has only a negligible "fade" with increasing jacket temperature. For instance the drop in octane number of the gasoline with 1 c.cm. of lead in going from 212 to 375 ° F. jacket temperature is only 1.5 octane numbers. These properties have been substantiated on a number of gasolines made by low-temperature hydrogenation.

The gasolines made by high-temperature hydrogenation have lead susceptibilities and "fading" tendencies midway between cracked and low-temperature hydro gasolines. (See Figure 1.)

Although the above has dealt with the low-temperature hydrogenation process when operated for maximum production of gasoline by recycling, it is possible to process feed stocks "once through" by this method, making gasoline of 60 to 62 octane number and high-quality export-grade burning oil (44 A.P.I. gravity and 400 viscosity) simultaneously. If preferred, gasoline and Diesel oils could be made simultaneously by this method. The burning oils produced in this way are finished by merely caustic or soda washing.

COMPARISON OF HYDROGENATION AND CRACKING RESULTS

To serve as a basis of comparison of the cracking and hydrogenation processes, five stocks have been chosen on which cracking and hydrogenation data are available. These stocks cover the range from refractory to paraffinic (aniline points 90° to 156° F.). Both high and low boiling and cracked and virgin gas oils are included. In a few cases actual hydrogenation runs had not been made on the gas oils in question; however, information on similar stocks permitted quite accurate estimation of results.

Table IV summarizes the operating conditions and products made from these five stocks by (*a*) cracking, (*b*) high-temperature hydrogenation and (*c*) low-temperature hydrogenation. It is evident from this compilation that:

(1) Both hydrogenation methods offer substantial increases in gasoline yields over cracking in all cases. Whereas cracking produces 90 to 95 volumes of liquid product (per 100 volumes of feed) of which usually 50 to 70 volumes are gasoline and the rest tar, hydrogenation yields 90 to 110 volumes of gasoline on the same basis.

(2) Higher conversions, as indicated by the per cent fresh feed, are realized with hydrogenation.

(3) Since only a caustic wash is required on the low-temperature hydro gasolines, negligible treating losses and losses of octane rating are encountered on these products.

(4) The octane numbers (Series 30 motor at 212° F. jacket temperature) of the cracked gasolines are in general higher than those presented for the hydrogenated products. This apparent advantage, however, is counterbalanced in large measure by the superior lead susceptibility and "non-fading" properties of the hydrogenated fuels. The results shown for the high-temperature hydrogenation process are based on the use of catalysts of the C-type (see Table I). Where higher octane

TABLE IV
Comparison of Hydrogenation* and Cracking† Results

Feed Stock:	1			2			3			4			5		
Type	Mixed Cracking Stock			Coastal Cycle Gas Oil			Heavy Naphtha Bottoms from Mixed Crudes			Mid-Continent Gas Oil (Light)			Mid-Continent Gas Oil		
A. P. I.	28.4			26.0			30.8			40.7			33.4		
Aniline Point, °F.	90			125			110			146			156		
50% at °F.	453			556			447			440			540		
% at 400°F.	20			—			22.7			16.0			—		
F. B. P., °F.	680			–			—			618			—		
OPERATING RESULTS	**Cracking**	**High-Temp. Hydrogenation**	**Low-Temp. Hydrogenation**	**Cracking**	**High-Temp. Hydrogenation**	**Low-Temp. Hydrogenation**	**Cracking**	**High-Temp. Hydrogenation**	**Low-Temp. Hydrogenation**	**Cracking**	**High-Temp. Hydrogenation**	**Low-Temp. Hydrogenation**	**Cracking**	**High-Temp. Hydrogenation**	**Low-Temp. Hydrogenation**
Total Throughput:															
Hydro, vol/vol./hr	—	4.0	2.2	—	4.0	2.2	—	4.0	2.2	—	4.0	2.2	—	4.0	2.2
Cracking, bbls./day	15,000	—	—	15,000	—	—	15,000	—	—	15,000	—	—	15,000	—	—
Vol.% Fresh Feed	31.5	46.0	72.0	38.0	42.0	67.0	32.0	59.0	76.0	43.5	76.0	81.0	35.0	55.0	70.0
Vol.-% 12° A.P.I. Tar on Fresh Feed (Cracking)	42.0	none	none	49.5	none	none	38.5	none	none	15.0	none	none	29.5	none	none
Gasoline (420°F. End Point):															
Vol.-% Raw Gasoline on Fresh Feed	50.5	93.0	110.0	44.0	92.0	110.0	54.5	91.0	109.0	72.5	89.0	108.0	61.5	91.0	109.0
Vol.-% Finished Gasoline on Fresh Feed	47.0	89.5	109.5	41.0	88.5	109.5	50.5	87.5	108.5	67.5	85.5	107.5	57.0	87.5	108.5
Octane No. at 212°F. of Finished Gasoline‡	78.5	74.0	64.0	72.2	67.0	58.0	75.5	69.0	60.0	68.2	64.0	57.0	69.6	63.0	54.0
Gasoline Production, bbls./day:															
(a) In a 5000 B/D Total Feed Hydro Plant	—	2060	3940	—	1860	3670	—	2580	4130	—	3250	4350	—	2400	3800
(b) In a 15,000 B/D Total Feed Cracking Coil	2220	—	—	2330	—	—	2420	—	—	4390	—	—	2980	—	—

*Recycle operation wherein the feed stock is totally converted to gasoline and a small amount of gas.
†Recycle operation to ultimate yield of gasoline and 12° A.P.I. Tar.
‡Octane numbers obtained on Series 30 motor at 212°F. and 600 R.P.M.

numbers are required catalysts A and B may be employed to advantage.

It should be noted that this comparison (Table IV) is based on gasoline of 420° F. end point from both cracking and hydrogenation. Neither the cracking nor hydro yields have been corrected for volatility, since it is assumed that the gasoline from either process would be blended off with other gasolines (usually straight-run naphthas) before marketing. The gasoline yields of the hydro process, and to a lesser extent those of cracking, may have to be reduced to meet the particular volatility specifications existing in different localities. In the following analysis an attempt is made to show the influence of volatility on the relative economy of the hydro and cracking processes.

BASES OF COMPARISON

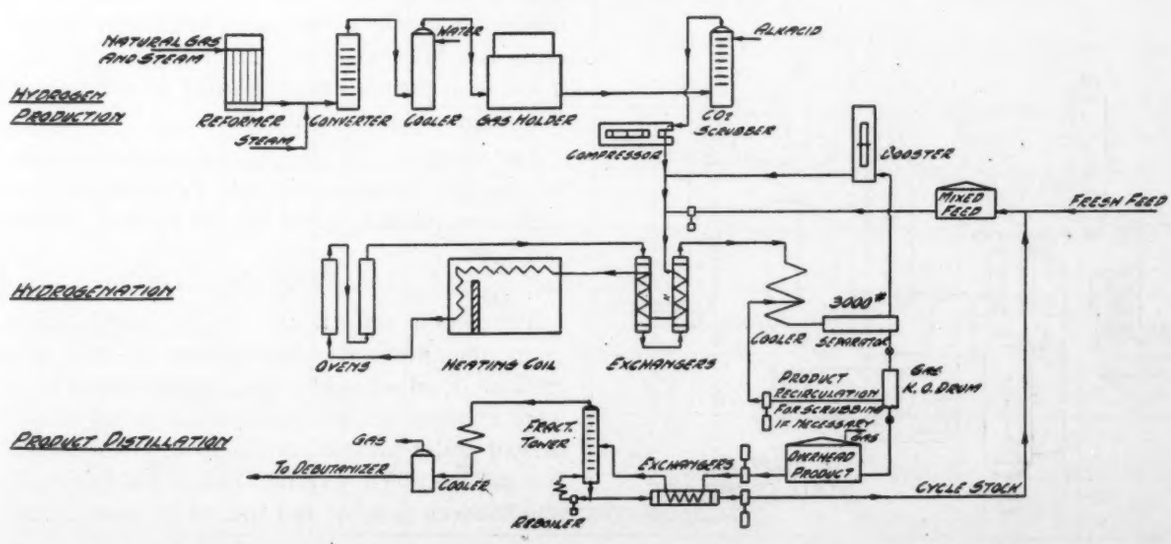
A. *Hydrogenation Plant.*

Experience gained on the operation of the commercial lube-oil hydrogenation units of the Standard Oil Company (New Jersey) and the gasoline hydrogenation units of the I.G. Farbenindustrie A.G. has indicated that certain simplifications and improvements can be made in hydro plant construction and operation. This comparison is based on a new hydro plant embodying these new design features. Some of the more important improvements and simplifications included are:

(1) Use of a structural steel enclosure for the reaction vessels and exchangers instead of a concrete stall.

(2) Simplified reaction drums of the type devel-

FIGURE II
SIMPLIFIED GASOLINE HYDROGENATION UNIT



oped by the Imperial Chemical Industries, Ltd., in its hydrogenation work. These changes have made possible a 20 per cent increase in reaction chamber volume and a reduction in the cost per unit volume of high-pressure reaction space.

(3) Employment of less expensive alloy steel tubing. The new alloy has been found to have satisfactory resistance to hydrogen and hydrogen sulphide attack in the commercial units of the I.G. Farbenindustrie A.G.

(4) Elimination of large excess capacity in the hydrogen producing units, since tests have shown them capable of higher throughputs than originally contemplated.

(5) Scrubbing of carbon dioxide from the exit gases from the hydrogen producing units at atmospheric pressure instead of at 16 atmospheres by employing the Alkacid Process recently developed by the I.G. Farbenindustrie A.G. This step accomplishes a 10 per cent saving in the amount of steam needed for gas compression.

(6) Elimination of considerable equipment for scrubbing recycle gases, by using overhead product as the scrubbing medium and by reducing the absolute amount of scrubbing.

A flow sheet of the simplified plant is presented in Figure 2. The unit may be used for either low-temperature or high-temperature hydrogenation by adjusting the reaction chamber temperature and by using different catalysts. In the low-temperature method all scrubbing of recycle gases may be eliminated.

With the addition of soda washing or doctor treating apparatus to the plant outlined in Figure 2, the low-temperature hydro gasoline leaving the hydro plant site requires no further treatment or finishing.

This comparison is based on a hydro unit having a total feed rate of 5000* barrels per day. This size unit has been chosen since it gives daily gasoline productions corresponding approximately with those obtainable on a modern cracking coil (see Table IV.).

It has been assumed that natural gas is available as a starting material for hydrogen production. In localities where natural gas is not obtainable, it would be equally satisfactory to substitute release gases from the hydro unit itself with a small increase in the plant investment for sulphur elimination. Refinery gases may also be used for this purpose if natural gas is not available.

Full engineering data on hydro plants for gasoline production are in the hands of I.G. Farbenindustrie A.G., Ludwigshaven am Rhein, International Hydro Engineering Company of The Hague and Hydro Engineering and Chemical Company of Elizabeth, New Jersey, U.S.A.

B. *Cracking Unit.*

Cracking costs are based on a modern high-pressure recycling cracking coil equipped with direct connected fractionating equipment. The general hook-up of the cracking unit is outlined in Figure 3. The total feed rate to the unit is taken as approximately 15,000 barrels per day.

C. *Octane Number Credits.*

In order to evaluate the different octane number gasolines produced by hydrogenation and cracking, the following system has been devised:

(1) Lead tetraethyl of the "Q" type recently made available in the U.S. by Ethyl Gasoline Corporation has been used as a basis of crediting octane numbers.

(2) An octane number † of 70 has been taken as a standard since this corresponds approximately with the octane number of most non-premium fuels marketed in the U.S.A. at present. All gasolines having an octane number below 70 have been given a debit for the amount of lead needed in bringing them up to 70. In making this debit cognizance has been taken of the specific lead susceptibility of the gasoline in question. Gasolines having an octane higher than 70 have been credited by assuming that they are blended with 60 octane number gasoline to give a final blend of 70 octane number. For each gallon of 60 octane number raised to 70 octane number, a credit of one cubic centimetre of lead tetraethyl has been allowed. In making this computation it has been assumed that blending of octane numbers in this range would be arithmetical.

For example, the 78.5 octane number gasoline made by cracking of stock 1, Table IV, received a credit of 0.85 c.cm. of lead/gallon on this method of evaluation.

D. *By-Product Credits.*

The worst uncertainty in the computation arises from the necessary inexactness of the by-product credits. Fuel oil, acid sludge and gas made by cracking were credited at the approximate prices which would prevail under present conditions at given market prices for gasoline. To a certain extent the basic price relation between gasoline and fuel oil is, however, subject to

* Obviously the use of larger units would offer considerable saving in both investments and running costs.

† Throughout this comparison octane numbers given are obtained on the Series 30 motor at 600 R.P.M. Insufficient data were available at the time of writing to correct to the new C.F.R. engine scale.

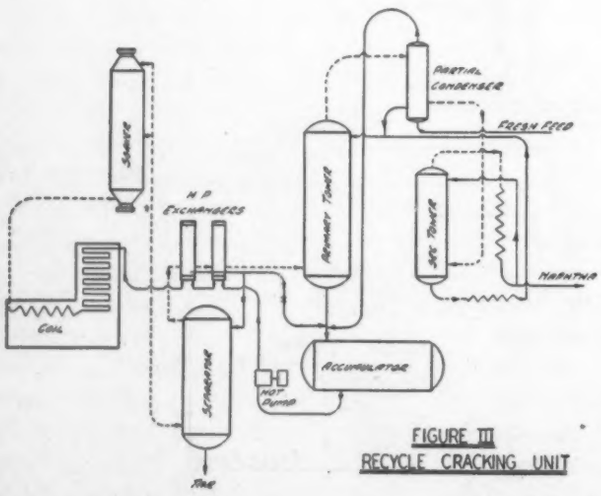


FIGURE III
RECYCLE CRACKING UNIT

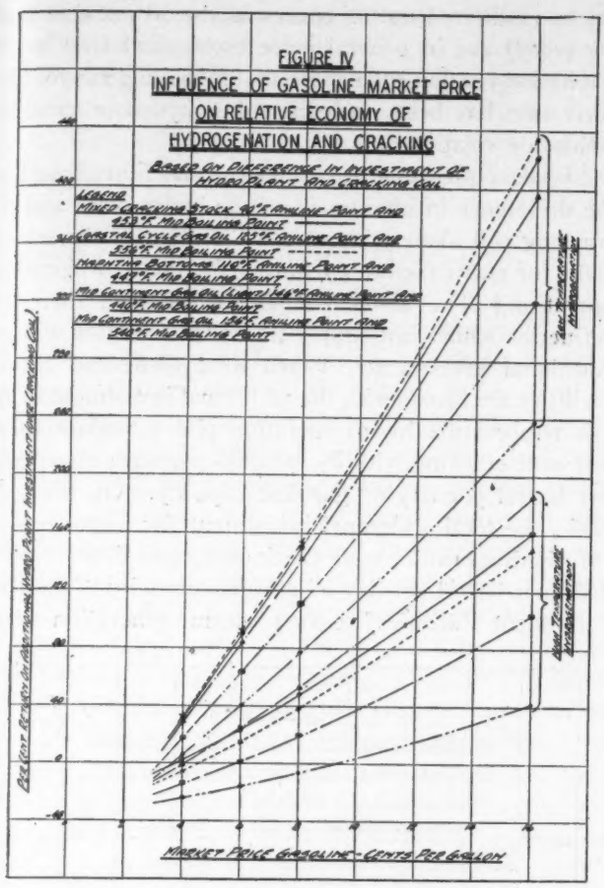


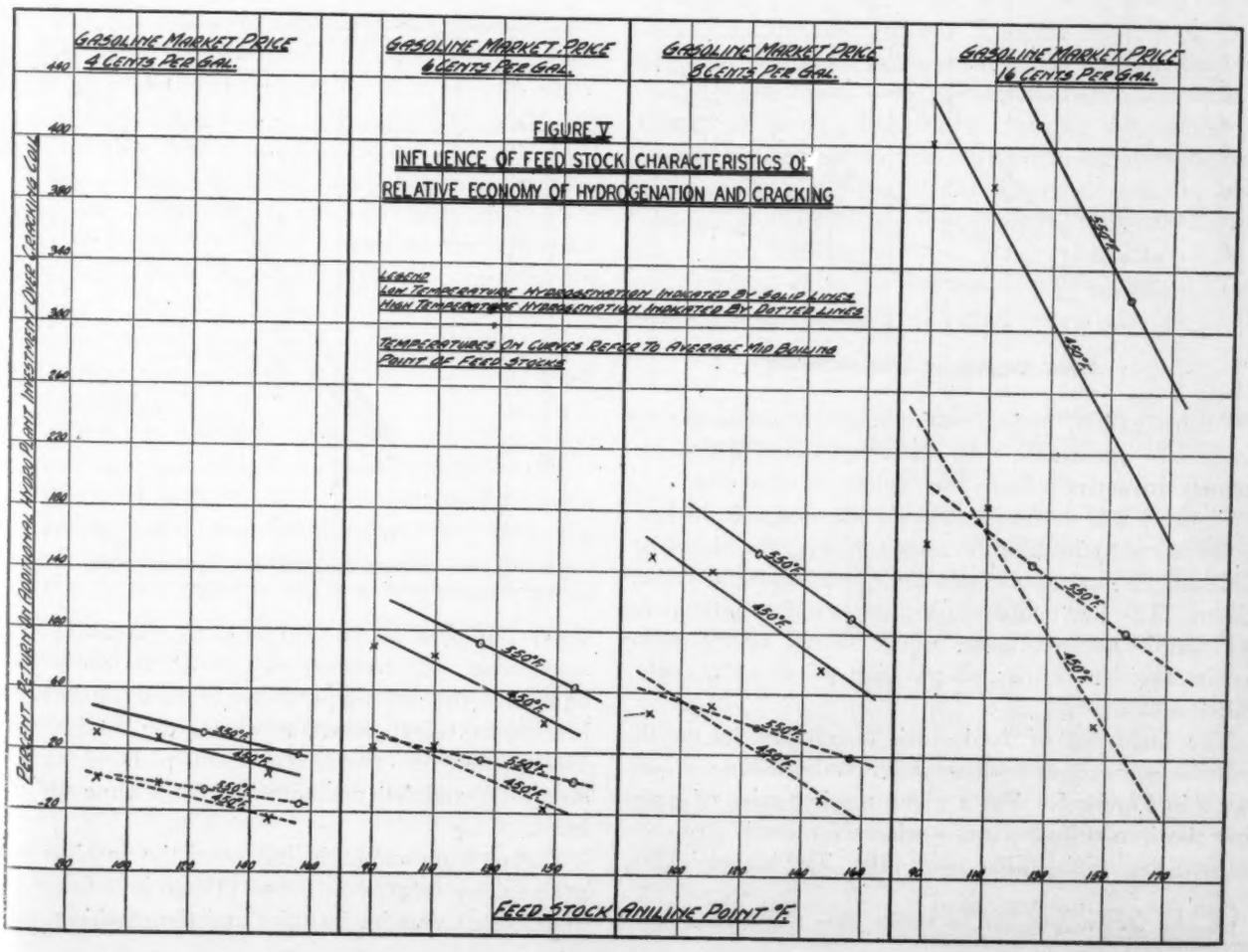
FIGURE IV
INFLUENCE OF GASOLINE MARKET PRICE
ON RELATIVE ECONOMY OF
HYDROGENATION AND CRACKING
Based on Difference in Investment of Hydro Plant and Cracking Coil
Leading
Mixed Cracking Stock 40° A. Aniline Point and 453° F. Mid Boiling Point
Coastal Cycle Gas Oil 103° A. Aniline Point and 534° F. Mid Boiling Point
Mid Continent Bottoms 116° A. Aniline Point and 487° F. Mid Boiling Point
Mid Continent Gas Oil (Cabbs) 144° A. Aniline Point and 440° F. Mid Boiling Point
Mid Continent Gas Oil 136° A. Aniline Point and 340° F. Mid Boiling Point
Low Temperature Hydrogenation
High Temperature Hydrogenation
Market Price Gasoline—Cents Per Gallon

alteration by extraneous factors. Since gas oil, the charging stock for both processes is an intermediate product the refinery value of which is fixed by its conversion values, the cost calculations were made to show the price which the two processes could pay for their charging stocks. Obviously the process returning the greatest value per gallon of charging stock (after due allowance for fixed charges) is the more profitable operation. Since, however, the hydrogenation process requires a greater investment than cracking for the same gasoline capacity, the profits or losses accruing to hydrogenation were expressed as the net return on the additional investment of the hydro plant ‡ over the cracking coil.‡ When using the low-temperature hydro method, this additional investment over cracking averages about $200 per barrel per day of gasoline capacity. For the high-temperature hydro method the additional investment ranges from $300 to $400 per barrel per day of gasoline capacity.

Plant costs used in this comparison are based on American construction and material costs. Operating materials and labor have been credited at a rate consistent with conditions in the average United States oil refinery.

It is believed that sufficient basic data are given so

‡ Facilities such as steam generation, water pumping, treating and rerunning plants not included here. In obtaining returns on investment the plant costs for each stock shown in Table IV are on the basis of equal daily gasoline capacity for the hydrogenation and cracking unit.

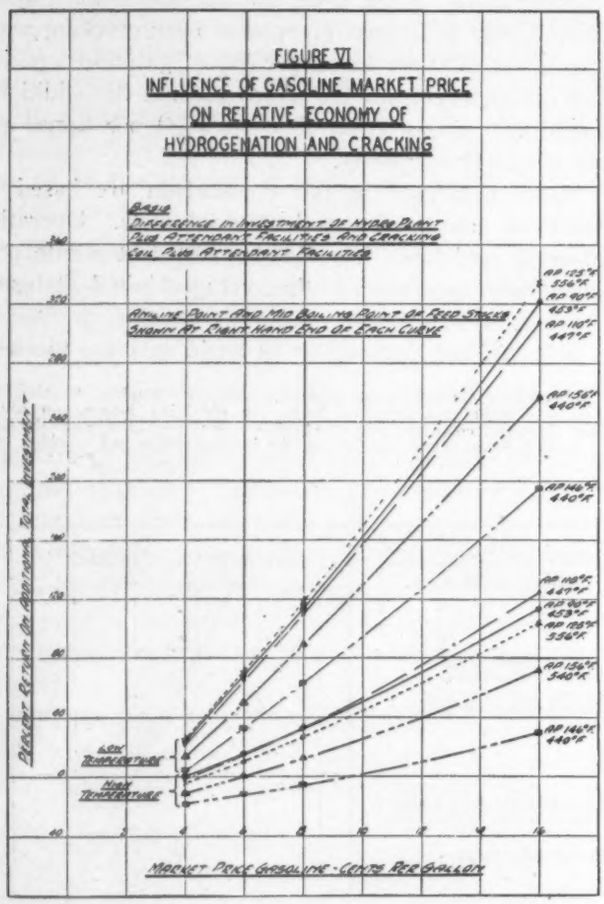

Gasoline Market Price 4 Cents Per Gal.
Gasoline Market Price 6 Cents Per Gal.
Gasoline Market Price 8 Cents Per Gal.
Gasoline Market Price 16 Cents Per Gal.
FIGURE V
INFLUENCE OF FEED STOCK CHARACTERISTICS ON
RELATIVE ECONOMY OF HYDROGENATION AND CRACKING
Leading
Low Temperature Hydrogenation Indicated By Solid Lines
High Temperature Hydrogenation Indicated By Dotted Lines
Temperatures On Curves Refer To Average Mid Boiling Point Of Feed Stocks
Percent Return On Additional Hydro Plant Investment Over Cracking Coil
550°F.
450°F.
Feed Stock Aniline Point °F.

that interested refiners in other parts of the world may make similar estimates for their own locality.

ECONOMIC POSITION OF THE HYDROGENATION PROCESS

A. *Influence of Price Structure.*

Figure 4 presents the results of the study of the relative economy of cracking and hydrogenation on the five stocks selected. This graph emphasizes the importance of gasoline market prices on the economic position of the hydrogenation process. At low gasoline prices (4 cents/gallon * gasoline and less) the hydrogenation process offers only a small advantage (in a number of cases a small loss) over cracking. At gasoline prices



7-9 cents/gallon, hydrogenation appears attractive on practically all stocks. At higher gasoline prices, extremely attractive returns are evident on all stocks.

Figure 4 also shows the decided advantage of the low-temperature hydrogenation operation over the high-temperature method at all gasoline prices above 3 cents/gallon. The low-temperature process offers returns on the additional investment, which should be attractive to the average refiner, at gasoline prices of 6 cents/gallon and above.

The influence of feed stock characteristics on the relative economy of hydrogenation and cracking is indicated in Figure 5. For a given market price of gasoline the low aniline point stocks offer more attractive returns than high aniline point oils. The higher boiling stocks (indicated on the curves as the 50 per cent boiling point) are in general more economical feed stocks for hydrogenation than those of low-boiling range. No correction has been made in either hydro or cracking yields for volatility.

The data presented in Figures 4 and 5 are based on the difference in investment of the hydro plant and the cracking coil alone without consideration of the investment for extra facilities required for the hydrogenation operation.† The above comparison is true, then, for refineries which can supply the extra facilities without additional investment. When total plant and service facilities are considered, the additional investment of the low temperature hydro operation plus attendant facilities over cracking with its facilities averages about $275 per barrel per day of gasoline capacity. On the same basis, the total additional investment for high-temperature hydrogenation over cracking ranges from $430 to $650 per barrel per day of gasoline capacity. The term "attendant facilities" covers steam generation plant,

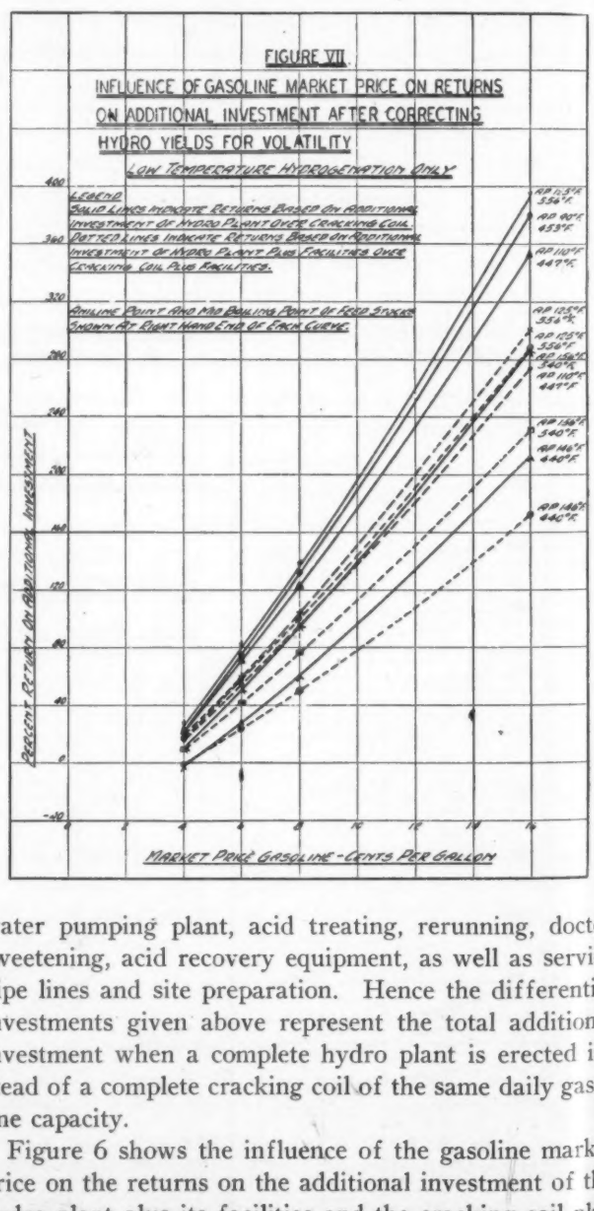


FIGURE VII
INFLUENCE OF GASOLINE MARKET PRICE ON RETURNS
ON ADDITIONAL INVESTMENT AFTER CORRECTING
HYDRO YIELDS FOR VOLATILITY
LOW TEMPERATURE HYDROGENATION ONLY
LEGEND
SOLID LINES INDICATE RETURNS BASED ON ADDITIONAL
INVESTMENT OF HYDRO PLANT OVER CRACKING COIL
DOTTED LINES INDICATE RETURNS BASED ON ADDITIONAL
INVESTMENT OF HYDRO PLANT PLUS FACILITIES OVER
CRACKING COIL PLUS FACILITIES
ANILINE POINT AND MID BOILING POINT OF FEED STOCKS
SHOWN AT RIGHT HAND END OF EACH CURVE
AP 125°F 356°F
AP 90°F 453°F
AP 110°F 447°F
AP 125°F 356°F
AP 136°F 340°F
AP 110°F 447°F
AP 146°F 440°F
AP 146°F 440°F
AP 136°F 340°F
PERCENT RETURN ON ADDITIONAL INVESTMENT
MARKET PRICE GASOLINE - CENTS PER GALLON

water pumping plant, acid treating, rerunning, doctor sweetening, acid recovery equipment, as well as service pipe lines and site preparation. Hence the differential investments given above represent the total additional investment when a complete hydro plant is erected instead of a complete cracking coil of the same daily gasoline capacity.

Figure 6 shows the influence of the gasoline market price on the returns on the additional investment of the hydro plant plus its facilities and the cracking coil plus

* All prices based on U.S. gallons.
† Normal plant depreciations for facilities have been included in the operating costs, however.

its facilities. A comparison of this plot with Figure 4 indicates that the return on the additional investment is somewhat less on this basis than when considering only the investments of the cracking coil and hydro unit alone. However, the general trends observed and the conclusions drawn are substantially the same for both cases.

B. *Influence of Changes in Low-Temperature Hydro Gasoline Volatility.*

Since refinery situations exist where the high yields by low-temperature hydrogenation cannot be realized due to inability to blend off the volatile hydro gasoline with gasolines deficient in light ends, the effect of reduction in volatility of the hydro gasoline has been analyzed. All low-temperature hydro gasoline yields have been decreased 4 per cent, which, based on data available, would ensure a finished gasoline without excessive volatility (per cent distillation plus loss not over 13 per cent at 140° F.).* The returns on the additional investment, for the five typical stocks, when using the lower yields are shown in Figure 7. Data are presented on the basis of the hydro and cracking coil investments alone as well as on the total investment inclusive of facilities. In general the returns possible with low-temperature hydrogenation are reduced somewhat by the correction for volatility, as may be seen by comparing Figure 7 with either Figure 4 or Figure 6.

The results of this study may be summarized as follows:

(1) The economic position of the hydrogenation process is markedly affected by gasoline price. At low gasoline prices hydrogenation offers no, or only small, advantages over cracking. High gasoline prices are favorable to the hydrogenation process.

(2) The low-temperature hydrogenation process appears more advantageous than the high-temperature process. It offers attractive returns on the additional hydro investment at a gasoline price of 6 cents/gallon and above.

(3) Low aniline point, high-boiling range gas oils and cycle stocks are the most attractive charging stocks for hydrogenation.

(4) In refinery situations where the high volatility of the low-temperature hydro gasolines cannot be utilized by blending off with naphthas deficient in light ends, some reduction in yield must be taken. This correction decreases somewhat the returns possible on the additional investment, although the low-temperature hydro process still looks attractive at gasoline market prices of 6 cents/gallon and above.

In evaluating the hydrogenation process its adaptability to a wide range of stocks and its convertibility to other operations such as lubricating oil improvement, water white production and hydrofining of cracked naphthas, should be considered. Moreover the hydro process manufactures a given quantity of gasoline from a smaller amount of feed stock than cracking. In a plant long on fuel oil, gasoline requirements can be met by processing a smaller amount of crude oil, when using hydrogenation, with an accompanying reduction in fuel oil. For example, the introduction of one low-temperature hydro unit in a typical refinery under study will reduce the crude oil requirements 14 per cent and drop the ratio of fuel oil to gasoline from 2.4 to 1.9.

The low-temperature hydrogenation process gives gasoline yields of high A.P.I. gravity and high volatility (40-50 per cent at 212° F.). In some refinery situations the use of hydrogenation would obviate casing-head purchases. Furthermore, this method of operation, since the gasoline produced requires only a soda or caustic wash, decreases or eliminates treating equipment, rerunning equipment and acid recovery plant.

COMBINATION OF HYDROGENATION AND CRACKING

Some of the more important combinations of hydrogenation and cracking which may prove of value to the refiner are as follows:

(1) Hydrogenation can be used on the refractory low aniline point stocks, allowing the cracking coils to run on the more paraffinic stocks which can usually be cracked with better conversions than the more aromatic gas oils.

(2) Hydrogenation of cycle stocks from cracking coils. Low-temperature hydrogenation is particularly effective in this regard since it can be operated once through to give gasoline and a gas oil of lower boiling range than the feed gas oil. This improved cycle stock can then be run in the cracking coils with higher conversions and lower coke formation. This combination will result in (1) lower cost cracking due to the increased conversion per pass, (2) increased yield of gasoline per barrel of crude, (3) decreased treating costs and (4) gasoline of higher volatility, lower sulphur and better gum stability.

The effect of a combination of hydrogenation (low-temperature operation) with cracking on gasoline yields,

TABLE V

Combination of Cracking and Hydrogenation as Affecting Gasoline Yields and Refinery Fuel Oil Production

Feed: Mid-Continent Gas Oil

Case	Barrels Gasoline by Cracking	Barrels Gasoline by Hydrogenation	Barrels Total Gasoline Per 100 Barrels Gas Oil	Octane Numbers			Tar Yields	
				Cracked Gasoline	Hydro-Gasoline	Total Gasoline	Per 100 Barrels Cracked Gasoline	Per 100 Barrels Total Gasoline
1	0	108	108	—	56	56	—	0
2	27.8	75.5	103.3	69.9	58	61	18.3	4.93
3	42.0	47.1	89.1	69.3	60	64.3	23.8	11.2
4	50.2	31.9	82.1	69.1	63	67	29.1	17.8
5	55.0	20.7	75.7	68.9	67	68.4	32.8	23.7
6	60	0	60	69.7	—	69.7	53.2	53.2

NOTES—(1) Case 2 represents once-through cracking, all cycle gas oil being sent to hydro units.

(2) Cases 3, 4 and 5 represent various and increasing degrees of recycling.

(3) Case 6 shows ultimate yield of gasoline as produced by complete recycling of gas oil in the cracking unit.

(4) Gasoline end points 400° F. in all cases.

(5) Low-temperature hydrogenation assumed in all hydro cases.

* Based on 420° F. end-point gasoline.

fuel oil production and octane numbers is presented in Table V. Cases 2, 3, 4 and 5 of this tabulation represents a situation in which a cycle gas oil from a cracking unit is hydrogenated. In all cases where hydrogenation is used increased yields of gasoline are obtained in conjunction with decreased fuel oil production. A comparison of Cases 5 (Cycle stock hydrogenated after intensive cracking) with Case 6 shows that this combination of hydrogenation and cracking accomplishes a 15.7 per cent increase in gasoline yield and a 50 per cent reduction in fuel oil production over complete recycle cracking.

(3) Low-temperature hydrogenation may be employed in conjunction with naphtha reforming. In this case the hydro process would be operated to give high yields of 420° F. end point gasoline. The heavy naphtha cut from this product could then be naphtha reformed by the once-through method outlined by Le Roi and Ferguson.[4] This combination would give high yields (90 to 100 per cent by volume on the feed gas oil) of excellent octane number and volatility gasoline.

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[1] Haslam and Russell: *J. Ind. Eng. Chem.*, Oct. 1930, **22**, 1030.
[3] Haslam and Russell: Paper presented at Eleventh Annual Meeting, American Petroleum Institute, Chicago, Ill., Nov. 13, 1930.
[2] Byrne, Gohr and Haslam: *J. Ind. Eng. Chem.*, Oct. 1932, **24**, 1129.
[4] Le Roi and Ferguson: Paper presented at the Tulsa Meeting of American Petroleum Institute, May, 1933.

Petroleum and Petroleum Gases as Chemical Raw Materials

(*Continued from page* 369)

by Peters and Kuster[74] to be a product of the reaction of a 1:1 mixture of methane and ammonia under the influence of an electric discharge at low pressure.

Petroleum derivatives themselves are claimed to have valuable fungicidal and insecticidal properties, but many insecticides consist of petroleum fractions as carriers for small quantities of more toxic substances such as pyrethrum extracts. Oxidized naphthenic and aliphatic petroleum hydrocarbons are claimed as insecticides and fungicides; similar claims have been made for emulsions containing alkali mineral oil sulphonates and white oils.

Water-soluble sulphonic acids of the unsaturated hydrocarbons of asphaltic-base oils have been suggested for use as protein precipitants in sewage or effluents.[75]

Wetting agents[76] are described in the patent literature, being produced by sulphonation of many substances, including oxidized paraffin wax or Russian petroleum and cracked petroleum fractions. Among the other processes including the use of petroleum fractions, there are patents[77] on the manufacture of synthetic tanning materials from mineral oils, and the production of keto-acids after the hydrolysis of the condensation products of such polycarboxylic anhydrides as phthalic anhydride with non-aromatic petroleum hydrocarbons in the presence of aluminum chloride. In the last case, from a petrol, phthalic anhydride, and aluminum chloride at 70-90° C., after hydrolysis with sodium carbonate and acidification, there is claimed a waxy keto-acid, the cobalt, etc., salts of which are driers for linseed oil, etc., and the bornyl and *iso*bornyl esters are plasticizers for cellulose nitrate. In recent patent claims[78] mixtures of mineral oils and fermented vegetable extracts blown with air are mentioned in a process for producing free fatty acids of high molecular weight, said to be suitable for soap manufactures.

The higher crude goes the more you save by not skimming it

Skimming makes straight-run gasoline and you can't make anything on it —it knocks

Skimming makes fuel oil, too, and there's too much fuel oil already—you're lucky if you can sell it at all

Dubbs cracking is the way to make gasoline—from fuel oil or any charging stock—volatile, anti-knock gasoline that holds old customers and makes new ones

Dubbscracking makes the biggest yield of the best gasoline from any charging stock at lowest cost—royalty and all

Universal Oil Products Co
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Dubbs Cracking Process
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SCIENCE AND TECHNOLOGY

Abstracts prepared in co-operation with the

REFINER AND NATURAL GASOLINE MANUFACTURER

by

THE LESLIE LABORATORIES

Traver Road, Ann Arbor, Mich.

under the supervision of

DR. E. H. LESLIE and DR. H. B. COATS

The abstracts here presented are selected from the current literature of science and technology to afford reference to fundamental information not easily available to all readers. Abstracts of articles appearing in readily obtainable trade journals are not included.

Photostat copies of original articles will be supplied at cost by the Leslie Laboratories. Complete or limited bibliographies covering special topics by title, by abstract, or in complete manuscript, will also be prepared and furnished at reasonable cost by the Laboratories.

Fundamental Physical Data

Vapor-Liquid Equilibria of Hydrocarbons at High Pressures. W. K. LEWIS & C. D. LUKE, *Ind. Eng. Chem.* **25** (1933) pp. 725-727.

Curves for the correction factor to be applied to the gas laws when dealing with hydrocarbons of more than 3 carbon atoms per molecule are corrected in minor details. The generalized fugacity plot has been correspondingly corrected. Preliminary data on the volatility of benzene in nitrogen at high pressures are presented. These are shown tentatively on the fugacity plot as a means of estimating the volatility of high-boiling hydrocarbons at high pressures. The correction factor for the internal energy of hydrocarbon vapors at low vapor volumes was determined by graphical integration from the isometrics of hydrocarbons for which sufficient data are available. The resulting corrections appear to be relatively independent of the temperature, at least over fairly wide ranges, and differences in the correction for hydrocarbons of more than 3 carbon atoms are probably small at corresponding reduced conditions.

Vapor Pressure of Low-Boiling Paraffin Hydrocarbons in Absorber Oil. G. L. MATHESON & L. W. T. CUMMINGS. *Ind. Eng. Chem.* **25** (1933) pp. 723-5.

A new apparatus was developed for the measurement of static vapor-liquid equilibria. Vapor pressures of n-butane, n-pentane, isopentane, hexane, and n-heptane from solution in a Mid-Continent absorption oil were determined over a wide range of concentration. All of these hydrocarbons showed a positive deviation from Raoult's law. The pressure deviations of the normal paraffins expressed as percentages of the value calculated from Raoult's law, were found to be approximately the same at the same molal concentration and temperature.

High Pressure Rectification. II. N-Pentane—N-Heptane System. L. W. T. CUMMINGS, F. W. STONE *and* M. A. VOLANTE. *Ind. Eng. Chem.* **25** (1933) pp 728-32.

Data on dew points and boiling points of solutions of n-pentane and n-heptane, for pressures of 6 atmospheres through the critical, are presented. Vapor and liquid densities at the two-phase boundaries were measured. Several isobaric vapor-liquid equilibrium diagrams were constructed from the data. Application of the data to the problems of high-pressure rectification is pointed out.

Vapor-Liquid Equilibria for N-Hexane—Benzene Mixtures. C. O. TONGBERG & F. JOHNSTON. *Ind. Eng. Chem.* **25** (1933) pp. 733-5.

Equilibrium data for solutions of n-hexane and benzene have been determined. N-hexane has been isolated from petroleum by close fractionation and removal of the benzene by nitration. It can be made by distillation of a n-hexane and benzene solution with tertiary butyl alcohol. Contrary to data in the literature n-hexane and benzene do not form a constant boiling mixture. However, enrichment of the vapor practically ceases at concentrations below 3.5 mole-percentage of benzene.

Measurement of the Thermal Conductivity of Mineral Oils. M. LOUIS and M. CARRETTE. *Ann. Des Comb. Liq.* **8** (1933) pp. 133-139.

The thermal conductivities of a spindle oil, a machine oil and a viscous oil were determined by a method in which heat flowed from a source at constant temperature through a layer of oil floating upon a layer of water. The underside of the water layer was in contact with a surface maintained at constant lower temperature. A steady temperature gradient is set up in 6 to 8 hours. The thermal conductivity of the oil can then be expressed in terms of the thermal conductivity of water. The conductivity decreases with increasing viscosity and for a given oil decreases with increase in temperature. The conductivity of the spindle oil was 0.00038 at 42°C and decreased to 0.00035 at 62°C. The results are estimated to be accurate to 10%.

Maximum Permissible Speeds of Flow in Gasoline Lines. B. MULLER. *Erdol u. Teer* **9** (1933) pp. 222-3.

The experiments of O. Sander, as described in a recently published book, dealing with the ignition of gasoline by static charges caused by high rates of flow through pipes are discussed. The results indicate that the maximum permissible speed is 4 meters per second.

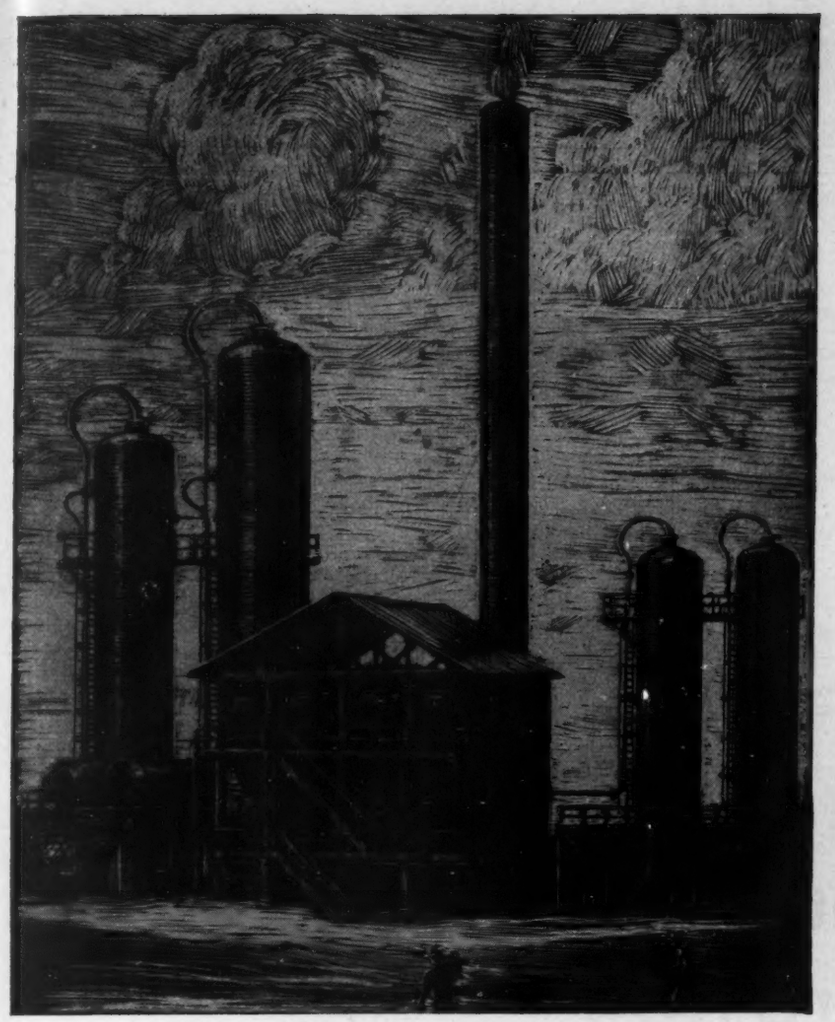
Chemical Composition and Reactions

Higher Aliphatic Compounds. III. Preparation of Paraffins. P. C. CAREY and J. C. SMITH. *J. Chem. Soc.* (1933) pp. 346-7; cf. C. A. **26** p. 2697.

Paraffins can be prepared by reduction of the iodide with zinc in acidic or propionic acid. A second method is the reduction of the iodide with zinc copper couple in ethyl alcohol. A third method is catalytic reduction with palladium calcium carbonate in propyl alcohol.

Chemical Composition of Petroleum. A. SACHANEN & R. WIRABIANZ. *Erdol u. Teer* **9** (1933) pp. 170-172, 187-189, 202-203, 220-222.

The article presents detailed studies of the petroleum from Grozny, Surachany, Balachany, Bibi-Eibat, Dossor, Kaluga and Perm. These oils were separated into twelve fractions of about 50°C. range up to 550°C. using vacuum distillation for the higher fractions. Specific gravity, refractive index and critical solution temperatures in aniline were determined for each fraction. Aromatics were removed with strong sulphuric acid and critical solution temperature redetermined. Petroleums may be divided into six main classes, according to their composition. Paraffin-base oils contain not less than 50% paraffins in the light-fractions and about 10-15% wax in the high boiling fractions. Above 300°C. there are more naphthenes than paraffins. Asphaltenes and resins are almost absent, and the aromatic content is small. An example is Pennsylvania oil. Completely naphthenic oils are rare; 50 to 80% naphthenes are contained in some fractions. Paraffin-naphthene base oils are common. The aromatic content is small and the wax content almost as high as the paraffin base type. Examples are Grozny and Surachany. Naphthene-paraffin-aromatic type oils are also widespread. They contain 1-2% wax and much asphaltenes and resins. Examples are Grozny (old field) and Bibi-Eibat. The naphthene-aromatic class is also common. Paraffins are practically absent



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Naturally, the selection of processes by the refiner should be established with reference to his existing refinery cracking equipment; plus a view to the advantages resulting from coordinated research, development, engineering and plant design. This means integrated progress.

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except in light portions. Aromatics may be contained up to 40% together with fairly large amounts of asphaltenes and resins. An example is Kaluga oil. The true aromatic crude with over 50% aromatic, for example, Perm oil, is seldom found. The paraffin-aromatic type is unknown. The paper presents many details.

Improvement of Petroleum by Catalysis. E. DEISENHAMMER. *Petroleum* **29** (1933), No. 17, pp. 3-4.

A Zistersdorf petroleum containing only 11.4% components distilling to 300°C. was distilled with .5% activated charcoal and then with a mixture of charcoal and silica gel. The distillate to 300°C. was increased from 11.4% to 45%. The benzene boiling to 200°C. was increased from 1.4% to 8.1%. Loss from gas formation was negligible. The activated carbon can be used repeatedly. Silica gel did not have the effect of increasing the yield of the product distilling up to 300°C.

Thermal Behavior of Sulfur Compounds in Hydrocarbon Solvents. II. Normal Butyl Sulfide in Benzene. W. M. MALISOFF and E. M. MARKS. *Ind. Eng. Chem.* **25** (1933) pp. 780-3.

The thermal stability of n-butyl sulfide in benzene solution was studied under varied conditions of temperature, concentration, and time. Results were shown to be reproducible. The products were mercaptan and hydrogen sulfide. Reaction rate was slow at temperature up to 450°C. In no case did reaction proceed to give more than 25.3% of hydrogen sulfide and 8.6% mercaptan. The reactions were found to be partly heterogeneous, and not the unimolecular reaction shown in the decomposition of the normal aliphatic mercaptans.

Pyrogenic Decomposition of Cyclohexane and of Cyclohexene in Presence of Silica Gel. A. MAILHE. *Chimie & Industrie* **29** (1933) pp. 759-65. ...

Cyclohexane begins to decompose at 600°C. and cyclohexene at about 550°C. in the presence of silica gel. Cyclohexane is first dehydrogenated to cyclohexene which, by further dehydrogenation, is converted into benzene on one hand and into an open chain hydrocarbon, presumably hexene. A series of olefins down to ethylene results from the decomposition of hexene. Propylene is the principal olefin product. At temperatures as low as 700° to 750°C. the olefins by several reactions form benzene, toluene, xylene, naphthalene, anthracene, and other complex aromatic hydrocarbons.

Preparation of Amyl and Hexyl Formate from Cracking Oils. E. SUCHARDA and T. MAZONSKI. (*Przemysl Chem.* **17** (1933) pp. 41-46.)

Low boiling olefines in cracked products can be converted almost quantitatively into secondary and tertiary amyl and hexyl formates by a process of continuous distillation, by which the distillate reacts in a side-tube with formic acid in the presence of sulfuric acid. The esters so formed are immediately returned to the distilling flask. By this procedure decomposition of esters by sulfuric acid and the polymerization of amylenes and hexylenes are reduced to a minimum.

Manufacture: Processes and Plant

Distillation and Fractionation Equipment. R. K. FISCHER. *Jour. Inst. Pet. Tech.* **19** (1933) pp. 529-38.

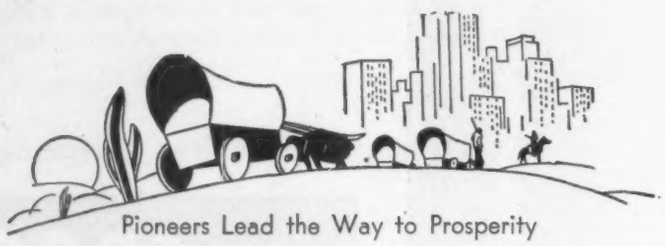
A review of distillation equipment and processes. Incomplete in scope.

Preventing Fog Entrainment in Continuous Distillation. A. E. BIRCH and H. M. WEIR. *Chem. and Met. Eng.* **40** (1933) pp. 366-8.

Attention is called to the fog-like entrainment in the vapor exiting at high velocity from a pipe still coil and the inability of any ordinary baffled entrainment separator to remove the fog. Entrainment was found to be approximately 1% on basis of the total vapor. The use of a centrifix centrifugal entrainment remover specially designed for the work resulted in eliminating two-thirds to three-quarters of the color of the overhead viscous stock taken as the first side-stream above the vaporizer of the fractionating column. Acid consumption in treating one typical stock was reduced from 85 pounds to 38 pounds per 50 gallon barrel. Loss was more than correspondingly reduced.

Production Facilities for Gasoline and Kerosene Distillates in the Baku and Grozny Refineries. S. N. OBRYADCHIKOV. *Groznenskii Neftyanik* **2** (1932) No. 9-10 pp. 32-40, and No. 11-12 pp. 60-5.

An analysis of the performance of a great variety of stills, such as old shell stills equipped with various bubble towers, and heat exchangers, as well as of the most up-to-date apparatus such as the Pintsch, Borrmann, Soviet,



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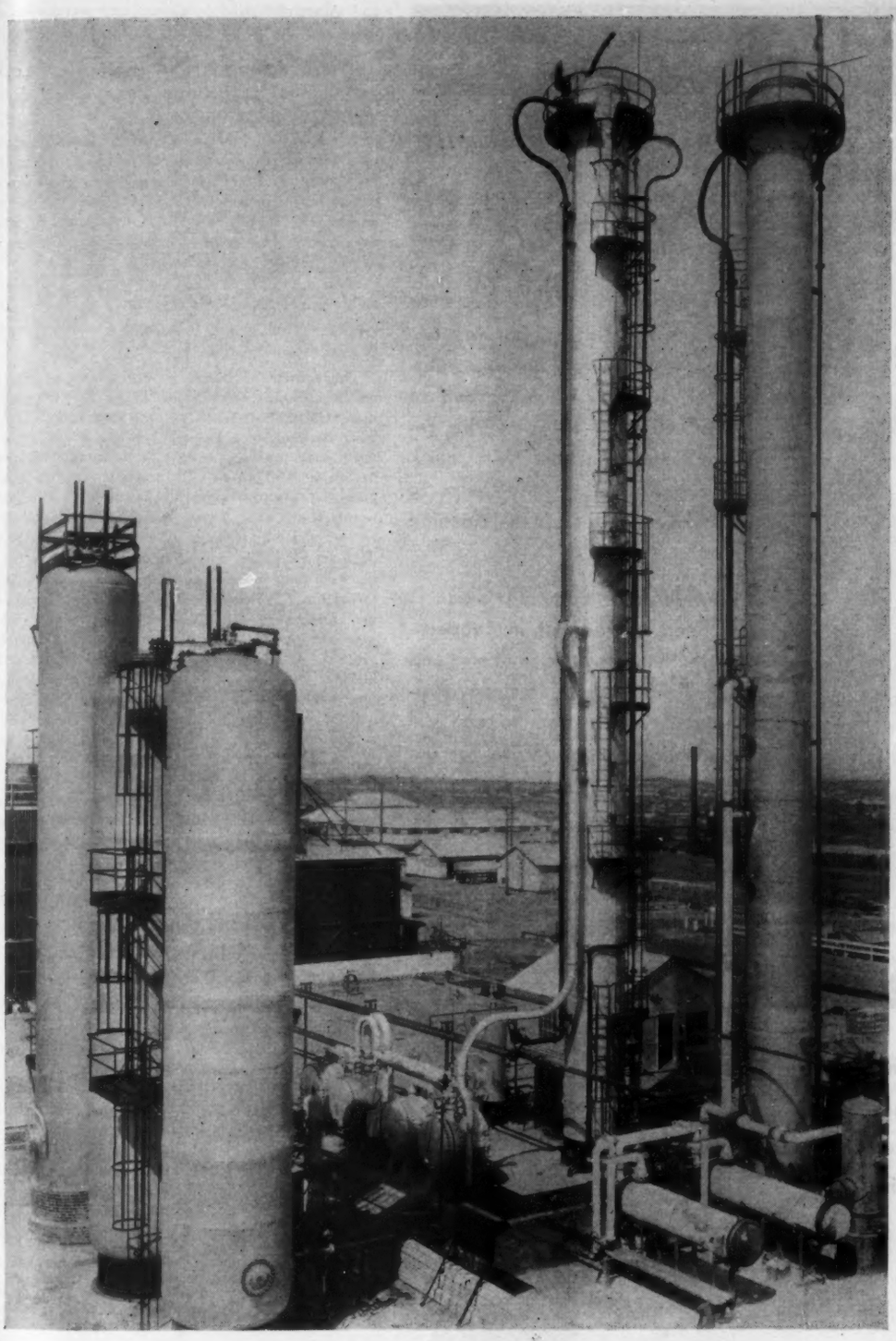

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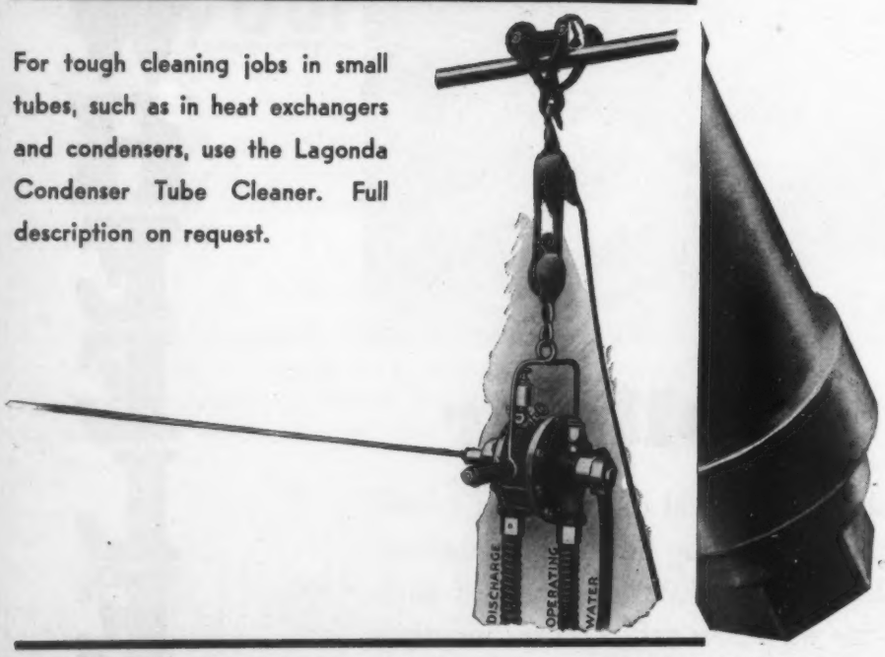

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and American stills is given, and recommendations are made.—A. A. Boehtlingk.

The Cracking Art in 1932. G. Egloff and B. L. Levinson. *Jour. Inst. Pet. Tech.* **19** (1933) pp. 504-28.

The trend of development of cracking, studies of cracking reactions, liquid vapor-phase cracking, vapor-phase cracking, cracking with oxidation, by-products of cracking and cracking equipment are reviewed. One hundred and twenty-nine references to the current literature of the subject are included.

Vapor-Phase Cracking. H. P. A. Groll. *Ind. Eng. Chem.* **25** (1933) pp. 784-98.

The subject of vapor-phase cracking is briefly reviewed and the mechanism of the reactions involved discussed at some length. Gaseous hydrocarbons and gas oil were cracked at atmospheric pressure over a wide range of temperatures and rates. Propylene was found to give the highest yield of aromatics. Striking regularities were found in the thermal treatments of all hydrocarbons. At all temperatures dementhanization was found to be more important than dehydrogenation provided carbon formation is avoided. The nature and yield of products were functions of temperature and rate throughout, and connected by a simple function over a wide range of conditions. A method of increasing the throughput of commercial plants is presented. On account of patent considerations most commercial processes include specific features, many of which are of doubtful advantage. Confusion and prejudice has arisen. The purpose of the paper is stated to be to clarify the situation by showing the inherent limitations of any vapor-phase cracking process and predicting results from any given change of conditions.

Inhibitors in Cracked Gasoline. II. Correlation of Inhibiting Action and Oxidation—Reduction Potential. C. D. Lowry, Jr., G. Egloff, J. C. Morrel and C. G. Dryer. *Ind. Eng. Chem.* **25** (1933) pp. 804-7.

The effectiveness of gasoline inhibitors as measured by an accelerated oxidation test is correlated with the critical oxidation potentials of these substances. The best inhibitors have potentials between 0.60 and 0.80 volts. Fair inhibitors show potentials of 0.800 to 1.043 volts. Compounds with higher potentials have practically no inhibiting value. Hydroquinone and some ethers show less inhibiting action than their oxidation potentials indicate. This is attributed to their direct oxidation.

Refining. W. J. Wilson. *Jour. Inst. Pet. Tech.* **19** (1933) pp. 497-503.

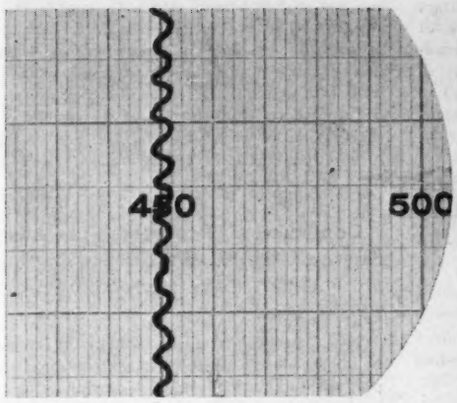
A report on the progress of refining during the last year in Germany, Poland, Roumania, Canada, India, Trinidad, and Peru.

Chemical and Physical Refining. B. C. Allibone. *Jour. Inst. Pet. Tech.* **19** (1933) pp. 539-48.

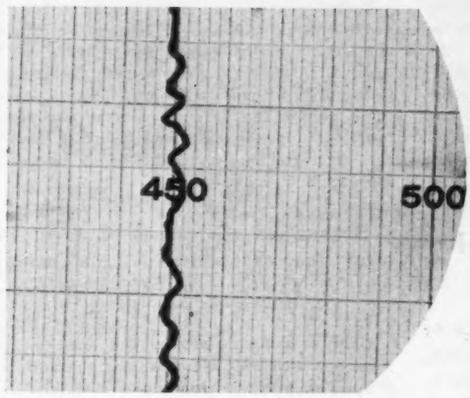
A review of published work on refining with acid, alkalis, and miscellaneous reagents, hydrogenation, heat treatment, vapor-phase treatment, zinc chloride, solvents, as well as solvent dewaxing. Sixty-six references are given.

Continuous Regulation of the Neutralization of Acid-Treated Oils. Bernard S. Greensfelder. *Petroleum Z.* **29** (1933) No. 13, pp. 6-8.

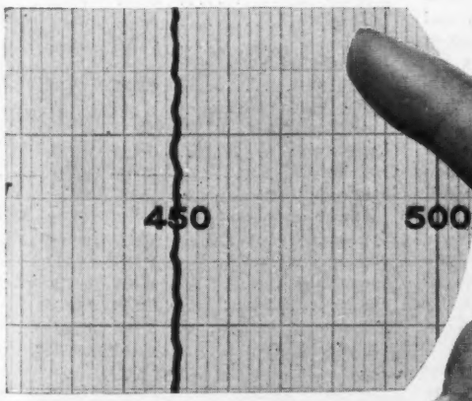
The continuous neutralization of light oil that has been refined with sulfuric acid is controlled



Curve Shows Character of Temperature Regulation Produced by Two-Position Control.



Better Temperature Regulation Produced by Three-Position Control.



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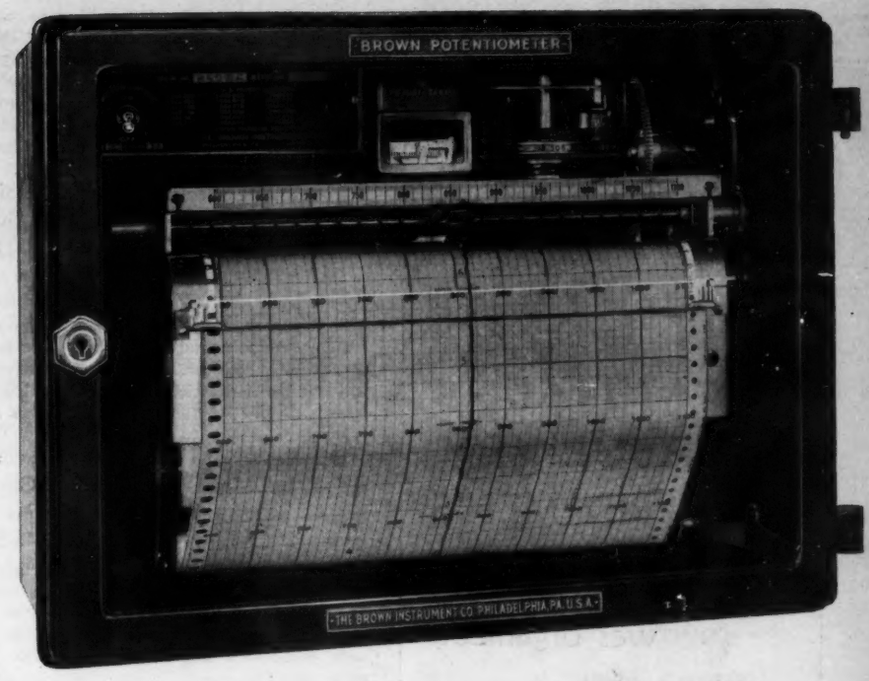

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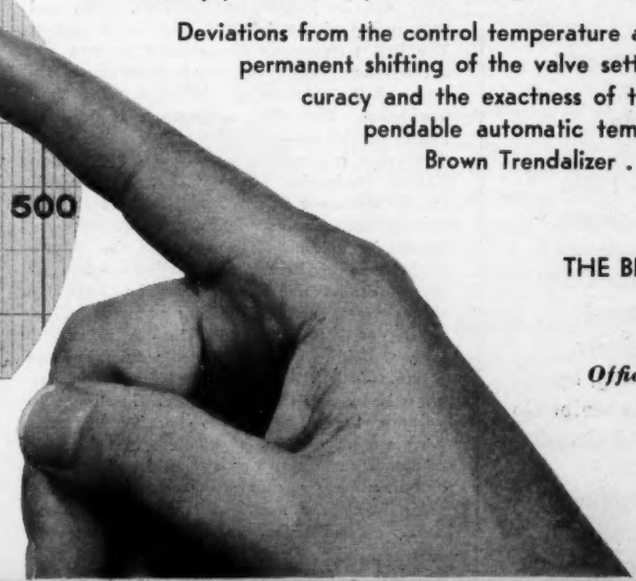

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by bringing the neutralized oil into contact with a solution containing 6 mg. per litre of methyl red and 25 mg. per litre of xylenol-blue. Green coloration shows a P_H value of 7.5-9. In this range the indicator shows a green color. With excess acid the indicator shows red and at P_H greater than 9 blue.

Treatment of Gasoline Containing Mercaptans with Alkali and Sulfur. F. R. MOSER. *Petroleum* Z. **29** (1933) No. 7, pp. 5-6.

Sour gasolines are sweetened by treatment with dry or aqueous caustic soda or powdered sodium carbonate and free sulfur. The product so obtained, however, is corrosive. The method will not be of practical importance unless combined with one for the removal of excess sulfur.

Oil Emulsions and Their Decomposition by Means of Electric Current. N. A. RYAZANOVSKII. *Groznenskii Neftyanik* **2** (1932), No. 11-12, pp. 45-52.

The Grozny oil emulsions are of hydrophobic type. A large number of experiments with varied electrical equipment are reported. An electrical de-emulsifier developed by the Grozneft (described in some detail) was finally adopted. The current used is 45 kilovolts and the consumption of current per metric ton of emulsified crude oil amounts to 0.3-0.4 kilowatt hour.—A. A. Boehtlingk.

Products: Properties and Utilization

Relation of Quality to Economics of Manufacture of Aviation Gasoline. G. G. OBERFELL. *Trans. Am. Soc. Mech. Eng.* (*Aeronaut. Eng.*) **5** (1933), No. 2, 79-87.

The quality of aviation gasoline at present controls the design of aircraft engines of the spark-ignition type. The essential properties of a good aircraft gasoline are volatility, vapor lock, antiknock and gum content. The volatility can be judged by the 10%, 50%, and 90% points of the A.S.T.M. distillation curves. The 10% temperature denotes easy starting and acceleration. The 50% temperature is a criterion of the warming-up and accelerating characteristics. The 90% temperature is an indication of the tendency to crank case dilution. The vapor pressure is mostly related to vapor-locking tendencies. The Reid vapor pressure can be estimated from the A.S.T.M. 10% evaporation temperature and the temperature at which the volume distilled equals the volume of butanes or lighter hydrocarbons found by actual composition analysis. The estimated values are within the limit of accuracy of the testing method, namely 0.5 lb. A change to higher Reid vapor pressures would improve aviation fuels. Knock testing of aviation gasoline is by means of the Ethyl Gasoline Corporation Series 30 motor. Paraffin hydrocarbons are more stable to changes in test methods than unsaturated or aromatic hydrocarbons and they are also more responsive to tetraethyl lead. With the use of increased jacket temperatures and higher engine speeds in testing indicate higher octane values for highly cracked gasolines than are actually the fact. Antiknock in aviation gasoline is controlled by segregation of stocks and by the use of tetra ethyl lead. All butane and part of the pentane must be removed. Gum formation is controlled by segregation of stock and by the use of inhibitors. Specifications of various aviation gasolines are reviewed.

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Combustion Processes in Aircraft Engines. H. K. CUMMINGS. *Trans. Am. Soc. Mech. Eng.* (*Aeronaut. Eng.*) **5** (1933), 65-73.

The 3 general types of combustion occurring in homogeneous mixtures of explosive gases are preflame oxidation, normal burning, and the explosive wave. The experimental evidence on combustion processes occurring in spark-ignition engines are reviewed. Oxidation was detected first optically by noting changes in absorption spectra and by analysis of samples taken from the combustion chamber. Developed pressures were measured, the flame path was followed visually, photographically and electrically. The elucidation of combustion phenomena is materially helped by a study of the spectra of visible radiation and the measurement of infra-red radiations. Such data as these permit the determination of the characteristics of pre-ignition and knock. However, the exact mechanism of the knock is still unknown.

Detonation of Narrow Cuts of Paraffin Base Gasoline. R. A. VIRAB'YAN and V. YA. GOVAKOV. *Groznenskii Neftyanik* **2** (1932) No. 11-12, pp 52-60.

Grozny straight-run paraffin base gasoline was separated into 5°C. cuts and the anti-knock properties of these cuts were investigated under standard conditions. The properties are given in the table below:

Fractions	Sp. Gr.	Boiling Points (Engler)	Octane Nos.
Iso-pentane	0.626	28-29	90
Pentane	0.634	35-36	65
Iso-hexane	0.672	60-64	70
Hexane	0.686	65-68	48
Hexa-methyl-cyclo-pentane	0.710	69-76	60
Methyl-cyclo-pentane-cyclo-hexane	0.728	71-75	71
Cyclo-hexane	0.735	82-86	80
Iso-heptane	0.717	91-94	54
Methyl-cyclo-hexane-ethyl-cyclo-penta-toluene	0.765	104-109	no dentoation
Heptane	0.726	96-98	38
Iso-Octane	0.735	112-117	45
Octane	0.738	122-126	30
Xylene-naphthenic	0.770	129-134	50
Octane-naphthenic	0.753	125-130	35

The elimination of fractions for the purpose of improving the anti-knock properties of Grozny gasoline was found to be too expensive. However, compounding with some of the Baku gasolines that are high in naphthenes was feasible from the commercial points of view. A large number of experiments with particular reference to experimental conditions and details are reported.—A. A. Boehtlingk.

Pressure Increases, Gas Oscillations and Noises Caused by Combustion of Fuels. WAWRZINICK. *Automobiltchn* Z. **36** (1933) pp. 73-8 and 136-42.

Explosions of hexane-air and Baku gasoline-air mixtures were studied in specially constructed bombs and internal combustion engines. The

increase in pressure, the ignition point, and the explosion noises, as well as the nature of the flame propagation, were measured by electrical devices free from momentum. The highest pressure in a bomb was observed upon the arrival of the flame on the bottom of the container. The highest flame velocity existed in the first stage of combustion in the area short of air. The explosion noise is noticeable before the flame touches the bottom. The time elapsed between the initiation of the noise recorded by the oscilograph and the maximum pressure is 20-30% of the time required for the passage of the flame through the space. The noises were of a strictly sinus type. A direct relationship between the length of the combustion chamber and the inverse Hertz number of the gas oscillation was established. The oscillations were 900-4000 Hertz. Photographs reproducing the oscillations are given and the results are plotted and tabulated.—A. A. Boehtlingk.

Introducing Water Into the Cylinders of Internal Combustion Engines. H. R. W. SCHREIBER. *Automobiltechn. Z.* **36** (1933), pp. 32-3.

Water introduced into the cylinders together with gasoline may give a temporary increase in power up to 35% as a result of the catalytic action of the walls. However, the corrosive properties, and the formation of scale, make its use impractical. The injection of water in some of the two-stroke boat engines primarily effects a cooling of the motor.—A. A. Boehtlingk.

Bitumen-Mineral Mixtures for Use in the Cold. W. BECKER. *Asphalt u. Teer,* **33** (1933) pp. 270-275.

For use in the cold the viscosity of bitumen is reduced with an oil to correspond to that of the bitumen at 180-200°C. Comparative properties are given for a petroleum bitumen and a tar residue of the same hardness. It is shown that the petroleum bitumen has definite advantages over the tar residue. For example, the ductility of the former drops from 150 to 0 cm. over 23°C. while for the tar residue a similar drop takes place at 2°. The properties of stone for admixture with bitumen are discussed.

Conradson Test for Motor (-lubricating) Oils. C. EHLERS. *Petroleum* **29** (1933), No. 19; *Motorenbetr.,* **6** 2-4.

Conradson carbon residue of blended oils of different viscosities increases with increasing viscosity. However, there is no correlation between the carbon residue of an oil and its behavior in the engine, and it is stated that the comparative value of oils, particularly when of varying origin, cannot be determined by means of this test. The carbon residue of an oil increases during the period of its use in the engine, and also increases on heating in the presence of oxygen in the laboratory.

Measurement of Color of Mineral Oils and their Individual Fractions. HANS MAGNUS. *Petroleum Z.* **29** (1933) No. 16, 11-12.

Reference is made to modern colorimeters that are supplied with devices to measure the color oils, even those of the darkest colors. Such measurements are based on Beer's law. This law does not hold for mixtures of different types of oils nor for those containing crystal matter or colloidal graphite.

Fractional Diffusion (Application to the Analysis of Fats and Mixtures of Hydrocarbons of High Molecular Weight). E. ANDRE. *Ann. des. Comb. Liq.,* **8** (1933) pp. 111-127.

An apparatus is described for the fractional extraction of a liquid. For example, of a fatty or mineral oil by a solvent with which it is immiscible. The oil is placed in a long cylinder which may be filled with fragments of glass tubing. The solvent is fed through the bottom of this tube. The more soluble portion of the oil dissolves in the ascending drops which collect in an upper layer, and the excess of solvent over a constant level is returned to a boiling flask. The solvent in this flask is changed at intervals. Each portion is evaporated separately, thus giving rise to a series of fractions of extracts. The method can be applied to the investigation of mixtures of hydrocarbons of high molecular weight, as, for example, mineral oils. It is particularly useful in studying the optically active components of these oils as racemisation can be avoided.

Critical Points of Solutions of Commercial Hydrocarbon Mixtures in Liquid Ammonia. H. TROPSCH and B. G. SIMEK. *Mitt. Kohlenforschungsinst. Prag,* (1931) pp. 62-73.

When hydrocarbon solution contains more than 50% of aromatics the critical solution temperature in aniline it cannot be used as a method of analysis on account of the low temperature required. Liquid ammonia can be used. The critical solution temperature of hydrocarbon mixtures in liquid ammonia were determined. An examination of benzene gasoline mixtures shows a close relationship between the ammonia and aniline points.

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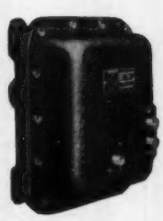

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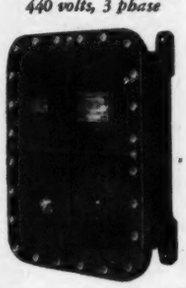

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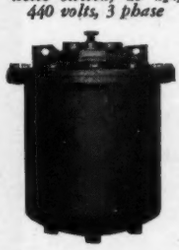

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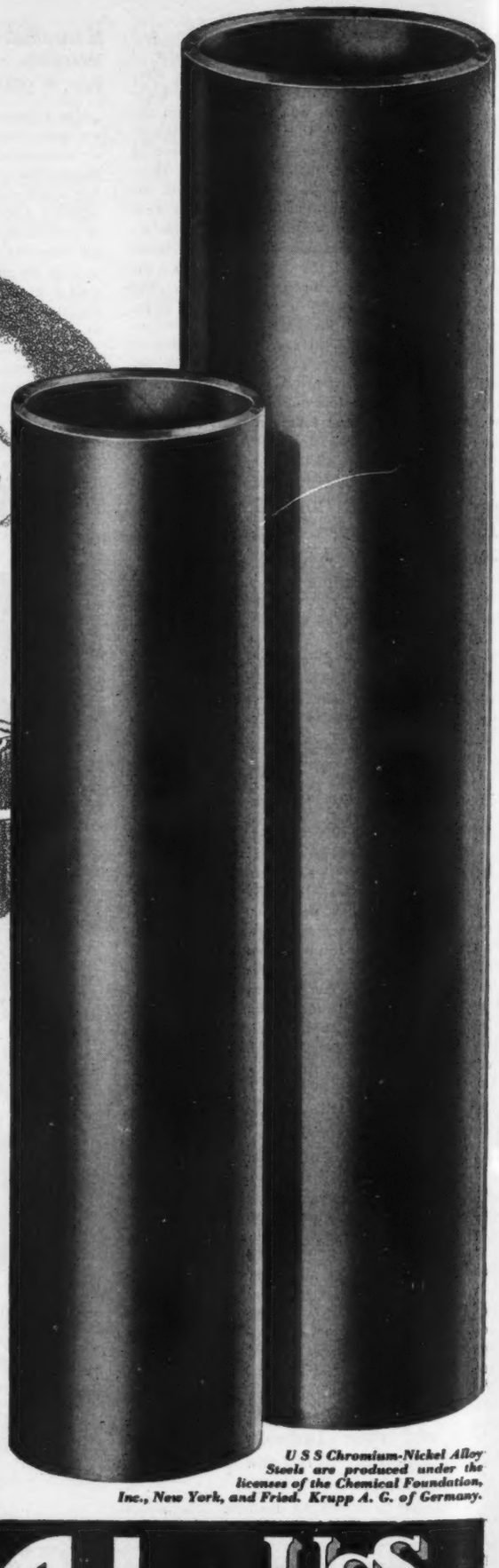

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THE MONTH IN REVIEW

Planning and Co-ordination Committee for the Industry

THE Code of Fair Competition for the Petroleum Industry was accepted and signed by Franklin D. Roosevelt, August 19, as a voluntary agreement under which the industry proposed to conduct its affairs after September 2. Following acceptance and signing, Secretary of the Interior Harold L. Ickes was named administrator of the code and shortly following that appointment the President named the industry's Planning and Co-ordination Committee. This consists of three men for the National Recovery Administration and 12 men for the petroleum industry.

Right hand man to Secretary Ickes and one of the three for the administration is James A. Moffett, who recently resigned as senior vice president of Standard Oil Company (New Jersey) to join in the administration work. Another for the administration is Donald R. Richberg, general counsel for NRA and long an attorney for organized railway labor and representative of labor on the NRA petroleum committee. Third for the administration is M. L. Benedum of Pittsburgh, identified with Benedum & Trees, Plymouth Oil Company and others.

For the industry the following were appointed: C. E. Arnott, president of Socony Vacuum Corporation; Howard Bennette, president of Western Petroleum Refiners Association; Axtell J. Byles, president of American Petroleum Institute; Henry M. Dawes, president of The Pure Oil Company; Wirt Franklin, president of Wirt Franklin Petroleum Corporation and of Independent Petroleum Association of America; W. T. Holliday, president of Standard Oil Company of Ohio; K. R. Kingsbury, president of Standard Oil Company of California; B. L. Majewski, vice president and co-receiver of Deep Rock Oil Corporation; E. B. Reeser, president Barnsdall Oil Corporation; Charles F. Roeser, president, Roeser & Pendleton; Ralph T. Zook, president, Sloan & Zook and Pennsylvania Grade Crude Oil Association, and Amos L. Beaty, director Phillips Petroleum Company, formerly head of The Texas Corporation and president of the American Petroleum Institute.

Economic Recovery Keynote for N. P. A.

SOUND Economic Recovery for the industry will be the keynote of the 31st annual meeting of the National Petroleum Association, at the Traymore Hotel, Atlantic City, September 20, 21 and 22. In the general sessions and group conferences the "Code of Fair Composition for the Petroleum Industry," will be the most important feature of the meeting.

Charles E. Arnott, member of the Planning and Coordinating Committee, will be the principle speaker on the marketing code. Representatives of the various refinery districts in which members of the association are located will participate in the discussion. Dr. Joseph E. Pogue will present his paper on Petroleum Economics and the present situation. Dr. Pogue has been engaged in economic studies for the NRA. A speaker from the NRA will discuss wage schedules in the oil industry and other industries.

The work of the American Petroleum Industries Committee will be discussed by Baird H. Markham, who has been identified with the industries work on taxation, both state and federal, for the past year. James H. Herbert, President of the Fire and Safety Marshals of the National Petroleum Association, will discuss the subject, "What Effect will the NRA have upon Fire and Accident Costs?" There will be a discussion of the modification of the anti-trust laws by the National Recovery Act. A speaker from the Ethyl Gasoline Corporation will discuss the development of "Q" compound and other related subjects. The group conferences will include studies of gasoline, lubricating oils, taxation, traffic, and the Code. The Fellowship Dinner will be held Thursday evening.

Annual Safety Congress and Exposition

The Twenty-Second Annual Safety Congress and Exposition will be held at the Stevens Hotel in Chicago from October 2 to 6. The General Chairman of the Petroleum Section sessions will be C. L. Hightower of Texas Pacific Coal & Oil Company; and the secretary will be H. N. Blakeslee of the American Petroleum Institute.

Steadily for the past three years the petroleum industry has been making good progress in accident control. For the year 1932, 101 industrial units, which had more than 565 million manhours of work, reported their accident experience to the National Safety Council. The average accident frequency rate of these companies dropped about 15 per cent in comparison with 1931, and their severity rates fell off about eight per cent.

Since 1926, with the exception of 1929, the accident frequency rates of the group of petroleum companies reporting to the council have steadily decreased, with a total reduction of nearly two thirds. The accident severity rates of these companies have not been so favorable. There were increasing accident severity rates up to 1929; and since that date there have been consistent reductions, the 1932 severity rate being about five per cent below the 1926 rate.

The interest in accident prevention work is indicated by the gain of over 40 per cent in the number of companies which reported to the National Safety Council for both 1932 and 1931, in comparison with companies which reported for both 1931 and 1930. Among the different sub-groups, best accident frequency rates were made by the marketing and manufacturing groups; with higher rates by the marine, natural gas and gasoline, and pipe lines; and the highest rates were reported by the producing group.

At the first program session of the Petroleum Section, on Tuesday morning, October 3, General Chairman C. L. Hightower will talk on "Looking Backward As We Go Forward." Other topics of this session will be: "The Accident Trend in the Petroleum Industry," by J. W. Myers, secretary, Annuities and Benefits Committee, Standard Oil Company (New Jersey); "Opportunities in Accident Prevention," by a speaker to be announced; "What Are Our Health Problems in the Petroleum Industry?" by a speaker to be announced; and election of officers.

The general subject for the Wednesday morning session will be "Refining and Marketing," with the following topics: "An Effective Accident Prevention Program for Refinery Operation," by W. P. Raymond, Jr., safety engineer, Standard Oil Company of Louisiana; "Problems in Handling Ethyl Fluid and Ethyl Gasoline," by Dr. Robert A. Kehoe, Ethyl Gasoline Corporation; "Controlling Accidents Among Marketing Department Employes," by A. J. Martinson, safety supervisor, Union Oil Company of California; "Safety for the Public in Sales Operation," by Captain A. J. Nicholson, superintendent, educational division, The Texas Company. The Thursday morning session will be de-

voted to the general subject of "Production." At the Thursday luncheon session, H. N. Blakeslee, secretary of the section, will discuss "Data on the 1933 Petroleum Section Contest." Also, an officer of the National Safety Council will present National Safety Council trophies and certificates.

The Accident Prevention Equipment Manufacturers' Section will have a special session on safety equipment. The important problem of motor vehicle safety, since many industrial plants have motor fleets, will be considered in the sessions of the delivery, taxicab and bus section, and the street and highway traffic section.

There will be a permanent exhibit, at the Stevens Hotel, of modern equipment for the promotion of safety and health in industry and in public places. This will include mechanical safety devices, protective clothing, modern first-aid kits and hospital accessories, and motor car control equipment.

The congress sessions have been so planned that delegates also will have opportunity to visit a Century of Progress, not far from the Stevens Hotel. In the Social Science Building on the Exposition grounds there is a permanent safety exhibit by the National Safety Council, in cooperation with the City of Evanston. Another permanent safety exhibit is the Rescue Car of the U. S. Bureau of Mines, near the Travel and Transport Building.

Service on Foreign Petroleum Technology

A MONTHLY review of petroleum technology, patents and the like as reported from various foreign countries has been initiated by Dr. A. A. Boehtlingk, 2720 Summit Terrace, Linden, New Jersey, formerly of Standard Oil Development Company's legal department library. The first review appears this month under the name "Foreign Petroleum Technology." It consists of abstracts of foreign patents and articles and includes a section containing original and translated articles on petroleum written by outstanding petroleum technologists of foreign countries. One of the features is to be a complete record (abstracts) of Soviet Russia patents on petroleum and translations of Russian articles of interest to people in the patent art and to research workers.

Since abstract service is available in French, English and German in existing publications of the American and English scientific societies, the new service will deal particularly with countries hitherto neglected such as Brazil, and other South Amercan republics, Scandanivian countries, Italy, Poland, Roumania, Portugal, Holland and Hungary.

Dr. Boehtlingk has for many years been an abstractor for Chemical Abstracts and other periodicals, and in his eight years service with Standard Oil Development Company in its research laboratory and patent department library he was instrumental in translating a number of books on petroleum technology among which was the recently published "Chemistry and Technology of Cracking" by Sachanen and Tilicheyev. In addition several articles by leading Russian technologists have been translated by Dr. Boehtlingk and have been published in The Refiner and various other American Journals and scientific magazines.

Literature service such as bibliographies, translations, searches, and the like covering various chemical and engineering subjects can be supplied on contract basis by special arrangement.

Plant for Recovery Of Bromine from the Sea

THE first manufacturing plant to be constructed on shore for the recovery of bromine from the sea is now being erected at Kure Beach, about 20 miles south of Wilmington, North Carolina. The plant will be operated by Ethyl-Dow Chemical Company, a new concern formed by Ethyl Gasoline Corporation and Dow Chemical Company.

The output will be utilized entirely by Ethyl Gasoline Corporation as a constituent of Ethyl fluid. The enterprise however, will result in a large increase in the potential production of bromides in the United States, affecting not only industry but the arts and also the national defense, as bromine is an essential ingredient of certain tear gases used in warfare.

The plant is being built in units, each having a monthly capacity of 250,000 pounds of bromides. To produce 500,000 pounds of bromine a month, it is necessary to process seawater at the rate of 26,000 gallons per minute for 24 hours per day. It is estimated that in one cubic mile of seawater there are about 600,000,000 pounds of bromine.

The latest process developed by chemists and engineers of Dow Chemical Company involves treating the seawater with enough chlorine to convert the bromides in the water to free bromine. This bromine is blown out of the seawater by a current of air. The air containing the bromine is then brought into contact with soda solution which absorbs the bromine, forming a concentrated solution of bromide-bromate.

New German Society For Oil Research

AMONG the newer developments in the German oil industry has been the founding and establishment of the new German Society for Oil Research, or as known in Germany, "Deutsche Gesellschaft fur Erdolforschung." It is an organization comparable in principle to the American Petroleum Institute or to the British Institution of Petroleum Technologists. The official founding dates of the association are May 8 and 9, of this year, and recently headquarters have been established at Dorotheenstrasse 40, N. W. 7, Berlin.

The active figure in bringing about this organization, and its present president, is Prof. Dr. L. Ubbelohde, of Karlsruhe. Although the society is privately organized and controlled, its first vice president is Dipl.-Ing. G. Feder, Secretary of State of the Board of Trade, a government official, and through whom the association gains governmental recognition and cooperation.

The first specific attempt to organize the various technical oil interests in Germany may be said to have its origin as early as 1907. In that year Prof. Ubbelohde attended and became secretary-general to the first meeting of the International Petroleum Commission, meeting at Bucharest. This was the first general European attempt at tackling standardization problems.

For the following seven years many papers were written and assembled by Prof. Ubbelohde and a second general meeting or petroleum congress was planned for September and October of 1914, to meet in Bucharest. The oil men of Europe evidently had no intimation of the impending war as notices were dispatched over Europe advising of the congress late in July of 1914.

Naturally very little was accomplished in the early reconstruction period following the war towards marshalling the various phases of oil technology in Germany or Europe at large. In 1931, however, at Zurich, the Congress of the International Society for Testing Materials, devoted one section to oils and lubricants. From the work of this section the International Petroleum Commission drew new life and inspiration. It was decided to establish sections of the commission in different countries and this has already been accomplished in Austria, Poland, Rumania and some few others. In Germany the section idea expanded into the organization of the "Deutsche Gesellschaft fur Erdolforschung."

The German association has grown

rapidly and has a membership of more than 250 individuals, 50 industrial firms, and 20 scientific institutions. The association has sections devoted to the following special subjects on oil: geology, geophysics, deep-drilling, manufactures, transport, import, legal questions, political questions, machinery, nomenclature, the coal and lignite and derivatives, and problems of gasoline, greases and asphalt. With the new and rapid developments now taking place in the German oil industry, the German Association for Oil Research takes a very important position for service to the oil industry and for the advancement of the technical oil sciences. It also takes place with its kindred institutions in America, England and other countries in forwarding the difficult but necessary task of standardizing methods and measures in the oil world at large.

Petroleum Congress Urges International Testing Standards

RESOLUTIONS passed during the meetings of the World Petroleum Congress in London, England, last month urged greater cooperation between petroleum technologists of the world in the standardization of nomenclature and with regard to testing methods, specifications on paraffin wax, Diesel fuels, motor fuels, and bituminous materials for road construction.

Triennial meetings of the World Petroleum Congress were agreed upon by those assembled and the next meeting place of the 1936 Congress will be decided upon by the Institution of Petroleum Technologists, London.

The congress approved methods of testing bituminous materials as outlined in a paper by C. F. Jackson, as suitable for international adoption. Because of limited experience with the evaporation test discussed by Jackson, the Congress agreed that only two tests should be included in specifications for such materials in different countries. These are: Viscosity at 25°C. (77°F.) using modified Redwood tar viscosimeter, and the A.S.T.M. distillation test D20-30 (modified) including penetration and melting point on the residue obtained.

In order to overcome difficulties arising from the use of different viscosity scales and to have available values directly applicable to the physical behavior of fuels, it was recommended that viscosities in fuel specifications be expressed in poises. Further, it was recommended that, as far as possible, cetene numbers be given

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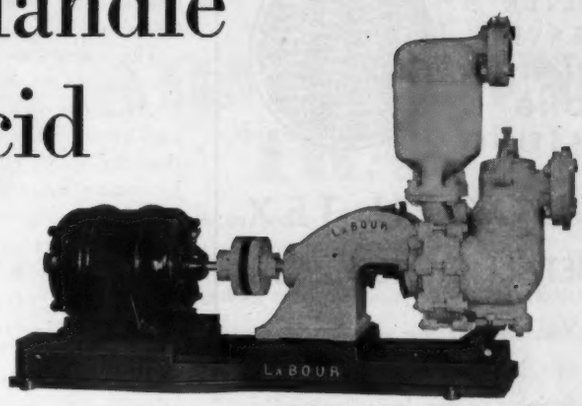

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for engine test results of ignition quality in addition to any other measure which may be appropriate to the method of test. The cetene number of a fuel is defined as the percentage by volume of cetene and a-methyl-naphthalene which has the same ignition quality as the same under test when tested under the same conditions.

The congress provisionally adopted the blends of iso-octane with normal heptane for providing fuels of standard anti-knock quality. In view of the fact that the C. F. R. engine has been used by many countries for only a short time, the congress felt that it is premature to recommend the C. F. R. Motor method as an international standard at present. It was recommended that intensive study be given the problem of knock rating with the broadest possible international cooperation and scope to the end that a method may be developed which may have world-wide acceptance. It was further recommended that in the forthcoming series of tests envisaged by the C. F. R. committee in the United States, further to check the suitability of the C. F. R. Motor method, contact should be made with certain other countries interested in different types of fuel, such as alcohol blends and blends rich in benzol, with a view of including these fuels in the test program.

In order to avoid overlapping and contradiction in the questions of international standardization of nomenclature and the methods of testing petroleum products, the congress expressed the wish that any proposals concerning international standardization should be made through the intermediary of the national standardizing bodies grouped under Committee I. S. A. 28.

▼ PLANT ACTIVITIES ▼

Solvent Process: Atlantic Refining Company, Philadelphia, is reported planning installation of a 10,000-barrel unit of its nitrobenzine solvent process for lubricating oil manufacture.

Cracking Unit: Big West Oil Company of Montana, at Kevin refinery, modernizing, dismantling shell stills and installing modern tubular furnace, a Dubbs gasoline reforming unit and Dubbs cracking unit. Ralph M. Parsons, consulting and contracting engineer. Capacity 1000 barrels.

Refinery: Lobitos Oilfields, Ltd., through action of its board of directors, announces intention to erect a refinery at Ellesmere Port, Manchester Ship Channel, England, where a site has been secured.

Refinery: Whitlash Refining Company, Shelby, Montana, organized by Henry McClarnan, E. M. Martin and Margaret Powers, plans erection of skimming plant.

Refinery: Transport Refining Company announced intention of drilling wells in the Hospah oil field, New Mexico, and to erect refinery at Baca, an enterprise which has been in reports several times during the past year. C. C. Worland, Chula Vista, California, is president; L. D. Welch, Los Angeles, secretary. Company has filed registration statements under the Federal Securities Act of 1933.

Repressure Plant: Humble Oil & Refining Company, Houston, to install natural gas repressuring plant in the Hilbig field, Bastrop County, Texas. Compressing system, estimated cost $75,000.

Solvent Plant: Union Oil Company of California, Wilmington, erecting propane solvent type lubricating oil plant.

Solvent Plant: Standard Oil Company (Indiana), Whiting, operating one propane dewaxing process unit, reported planning additional installations at one or two other refineries. Also additional installations of the company's Chlorex (dichlorethyl ether) solvent process are contemplated.

Distillation Unit: Pennsylvania Refining Company, Titusville, has let contract to Arthur G. McKee Company for new distillation equipment to supplant equipment to be dismantled on site of "cheese box" stills which have been in service 58 years.

Refinery: The La Canada, Ltd., reported let contracts for refinery at San Diego, California. B. C. Morrison, president; A. M. Pearis, vice president; H. M. Wright, treasurer.

Gasoline Plant: Gregg-Tex Gasoline Corporation has started construction of its 60,000,000-foot gasoline plant, Willow Springs, East Texas, installing four 400 horsepower Clarke double acting compressors. Contract to Petroleum Engineering, Inc. (Refiner, May, 1933, page 42a.)

Bromine Plant: Ethyl-Dow Chemical Company, jointly owned by Ethyl Gasoline Corporation and Dow Chemical Company, building at Kure Beach, 20 miles south of Wilmington, North Carolina, plant for recovery of bromine from sea water.

Gasoline Plant: Gilmore Oil Company of Los Angeles, plans erection of gasoline plant on property of El Clare Oil & Gas Company and Tehama Petroleum Company, located in Northern California. Contingent upon development of sufficient gas production.

Stabilization System: United Gas Corporation, Houston, contract to Petroleum Engineering, Inc., associated with Arthur G. McKee Company, for erection of 30,000-gallon stabilization unit at its Myrtis, Louisiana, gasoline plant.

Stabilization System: Chalmette Petroleum Corporation, New Orleans, contract to Petroleum Engineering, Inc., for vapor rectification type gasoline recovery plant at the Chalmette refinery.

Refinery: The Administrative Control of National Petroleum, Mexican Federal Agency, announces securing permit from Mexican govern-

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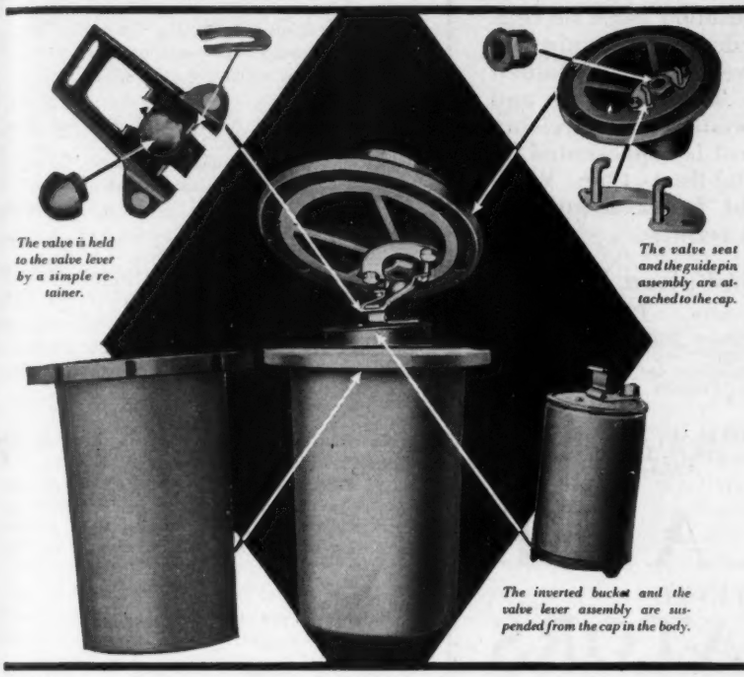
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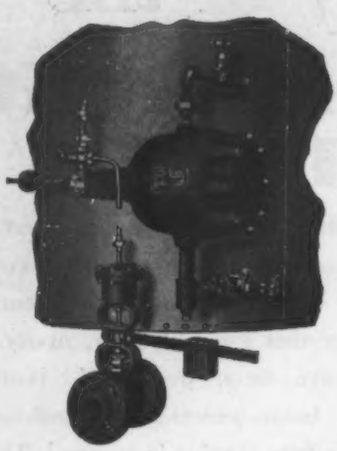

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ment to build a 2000-barrel refinery at Atzcapotzalco to cost $150,000 to $225,000, to operate on federal oil reserves production, and to be completed this year.

Distillation Unit: Sloan & Zook Refining Company, Warren, Pennsylvania, has awarded contract to Struthers-Wells Company, Warren, for construction of a 1500-barrel distillation unit. An earlier report erroneously credited this contract to Alco Products, Inc.

Rebuild: Lion Oil Refining Company, Ed Dorado, Arkansas, plans rebuilding damage to stills caused by fire, estimated at $50,000.

Refinery: Swift Current Oil Refining Company, Swift Current, Saskatchewan, Canada, plans erection of skimming plant. Estimated cost $40,000. Geo. Bremner in charge.

Refinery: Wentworth Refineries, Ltd., Burlington, Street, Hamilton, Ontario, Canada, plans erection of skimming plant. B. V. Hole, 159 Bay St. Toronto, engineer in charge.

Refinery: Swift Oil Company, Ltd., Mimico, Ontario, Canada, reported planning construction of skimming plant.

Gasoline Plant: M. Merriweather of Los Angeles, or care Chamber of Commerce, Calgary, Alberta, Canada, reported heading syndicate planning construction of gasoline plant and carbon black plant, Turner Valley field, Alberta, according to reports of the Department of Commerce.

Enlarge: Pure Oil Company, Van, Texas, adding two compressor units, rated at 750,000 cubic feet of gas daily, at the Van field natural gasoline plant. Brings total to 21 compressor units.

Refinery: Charco Redondo Refining Company, Mirando City, Texas, erected small skimming plant. H. C. Rogers, M. C. Riser and W. C. Bob, organizers.

Refinery: Spartan Refining Company, Pampa, Texas, erecting skimming plant eastern Gray County. Company formed by A. T. Parten, L. R. Hartwell and R. C. Sowder.

Refinery: Dixie Oil & Refining Company, Jackson, Mississippi, started operating skimming plant near Jackson. Ed. H. Condon in charge.

Gasoline Plant: Cargray Corporation, Amarillo, Texas, constructing 75,000,000 cubic foot Tulsa Type absorption gasoline plant, Carson County, in N½ SE Section 46, Block 4, I.&G.N. Ry. Survey. V. F. Taylor, Indiana, Pennsylvania, president and D. D. Harrington, Amarillo, vice president and general manager.

Purchase: Black Gold Refining Corporation, San Antonio, has been formed to take over and operate 500-barrel lubricating oil plant, Hondo, Texas, originally erected by Golden West Oil Company, and later known as Hondo Oil & Refining Company. Organizers of the new company are Carl Nelson, E. A. Berg and R. Y. Berg.

Refinery: Benco Refining Company, Three Rivers, Texas, erected small skimming plant. Company formed by A. C. Benson, Jack Montgomery and Henderson Coquat.

Rebuilding: The Texas Company has started rebuilding its Huntington Beach California natural gasoline plant, to complete in about six weeks at estimated cost of $100,000.

New Equipment for the Modern Plant

1. Thermometer and Pressure Gauge

THE BROWN INSTRUMENT CO.

The Brown Instrument Company, Philadelphia, has introduced a new and improved line of 8- and 12-inch circular chart instruments. These instruments include thermometers in indicating and recording types for temperatures from minus 40°F. up to 1200°F., and indicating or recording pressure and vacuum gauges for ranges from 10 inches of water up to 5000 pounds. All types are available in one-, two-and three-pen models. In developing this line of thermometers much research was devoted to improving the helix mechanism (Bourdon tubes). The mercury filled helix is built of a special stainless steel which stands 100 per cent over load and provides a surplus power to move the pen, it is said. The gas and vapor type helices are made of heat treated phosphor bronze, giving increased ruggedness and power.

Brown Gauge

In the pressure and vacuum gauges, three types of actuating movements are employed. For ranges 10 inches of water to 30 pounds, a flexible metal diaphram is used. For ranges 30 and 200 pounds, a spring-opposed bellows has been developed giving a powerful pen action in this range. For pressures over 200 pounds a helix is used. An electric clock eliminates hand winding where A. C. current is available. Cases are of die cast noncorrosive aluminum, interchangeable for back or bottom connection or for flush panel mounting. Other new features include a handy toggle switch to start and stop electric clock; combination door handle and built-in-lock; automatic chart clips carried on door hold chart in place; no chart knob to move as the chart is simply pressed on the chart hub; automatic pen release lifts pen from chart when door is opened; greatly increase torque eliminates pen friction; zero adjuster is rugged and accessible; convenient micrometer thumb screw permits easy recalibration, if range of instrument is to be changed after installation.

2. Steam Traps

THE STRONG, CARLISLE & HAMMOND COMPANY

The Strong, Carlisle & Hammond Company, 1392-1394 West Third Street, Cleveland, Ohio, announced the "80 Series" Inverted Bucket Steam Traps, which are claimed by the manufacturers to incorporate features which overcome several of the serious problems in steam trap practice. Two features of these new traps are the method of retaining the seat in place and the anti-balancing device. Instead of screwing the seat directly into the trap cover or seat holder, the seat in the new trap is forced against a gasketed surface by a brack, which is held tight against the cover by two stud bolts. By simply removing the two nuts from the studs, the bracket and seat may be lifted out. The feature is claimed to eliminate the use of special tools and possibility of damaging the seat or the cover during replacement. The anti-balancing device consists of a valve arrangement on the bucket which automatically varies the air vent opening during the cycle of operation. This device is claimed to practically eliminate the tendency to balance any dribble on varying loads or pressures. The traps are built of semi-steel construction for low and medium pressures and of forged steel construction for higher pressures and super-heat service.

3. Flow Controller

INTERNATIONAL FILTER COMPANY

International Filter Company, 59 East Van Buren Street, Chicago, has developed an improved flow controller, called Type CD, for use in industrial water plants where a uniform rate of flow is necessary or desirable. The controller consists of a venturi tube for measuring the flow rate, in combination with a hydraulically actuated valve and a pilot-controlled "Actuator." Operation of the controller is as follows: The differential established by the venturi is transmitted by a small by-pass flow to the two sides of a balanced diaphragm which is connected to the pilot valve. This flow passes through two constant orifices in the diaphragm. Should the flow increase, the diaphragm will be forced upward, while a decreasing flow will cause it to move downward. In either event, the control pilot will admit pressure water to the control valve cylinder, thus maintaining the valve opening at a point which will just keep the diaphragm at its balanced position. The flow rate is readily adjusted by varying the size of the variable orifice.

4. Barrel Filling Device

S. F. BOWSER & COMPANY

S. F. Bowser & Company, Fort Wayne, Indiana, has adapted its Xacto meter to the problem of facilitating and increasing accuracy of barrel and can-filling operations in the packaging of oils and similar products. The meter attains precise displacement by what is known as the "strike measure" principle. Five cylinders, each holding 0.1 gallon, when full, contain pistons driven from below by a wobble plate. At the precise instant when any one of

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REFINER AND NATURAL GASOLINE MANUFACTURER,
Houston, Texas, U. S. A.

Please see that I am supplied, without obligation, additional information on New Equipment Items Nos. .....described in September, 1933, issue of REFINER.

Name .....

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the pistons reaches its bottom dead center, a circular valve plate slides across the open upper end of the cylinder cutting off the inlet and insuring an exact quantity of fluid within the cylinder. By means of an easily read dial, the stroke of the pistons may be regulated exactly to secure the delivery of a definite volume at 60°F. regardless of temperature or specific gravity variations. This meter is available in various styles with volume totalizers, volume indicators or package totalizers and various filling auxiliaries. It is also built in a smaller and simpler type for the filling of small standard packages.

5. Safety Valve

CONDENSER SERVICE & ENGINEERING COMPANY, INC.

Condenser Service & Engineering Company, Inc., 310 Twelfth Street, Hoboken, New Jersey, announces development of the Jer-Stan Safety Valve, which the manufacturers state was perfected by the engineering department of a major refining company. The valve uses a frangible rod with section area dimensioned to break at a designated pressure and repeated tests are said to show that the frangible rod breaks with an accuracy of one per cent of designed load. There is included, between two sections of the valve a gasket of material to suit liquids or gases in the pressure vessel, which gasket may be of lead, monel metal, copper, etc. The Gasket assembled with the frangible rod and disc, is assembled to form a joint between the upper and lower halves at the valve body, and seals the pressure in the upper half. Before the rod breaks no shearing stresses are taken by the gasket because of its elasticity. After the frangible rod breaks, the gasket shears clean on the disc circumference at 1/6 of the designed pressure required to break the frangible rod. Bumper lugs cast in the lower half of the valve, support the valve disc after the frangible rod breaks, and as the disc rests on the lug the gases or liquid passes around the disc and through the outlet hole at the bottom into the atmosphere.

OUTLET FURNACE TEMPERATURES HELD WITHIN ¾° — 1° ±

New Taylor Dubl-Response Temperature Regulator maintains control during 24-hour run despite load changes

HERE'S another instance of unusual temperature control by the new Taylor Regulator. More proof to strengthen the belief that this instrument is one of the most important developments ever offered for temperature regulation in the oil and gas industry.

In the above installation the Taylor Dubl-Response maintained uniform outlet furnace temperatures by throttling the valve in the gas supply to the burners. During the 24-hour run the plant was switched from stabilizer gas to gas from another point, and back again. Temperatures were held within ¾° —1° plus or minus, despite great difference in B.T.U. content.

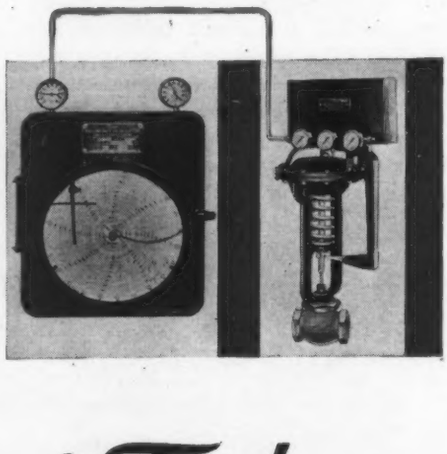
Wherever this new development has been installed—in stabilizers, towers, stills—it has successfully maintained uniform control despite load changes, process time lag, and varying operating conditions.

It overcomes stuffing box friction—eliminates "sticky valves."

It maintains straight line control automatically, eliminating manual adjustments during load changes.

It eliminates hunting. Assures throttling valve action.

Write for special Taylor Bulletin on this new Regulator and see how easily and quickly it can be applied in your plant. Send today to Taylor Instrument Companies, Rochester, N. Y., or to our Branch office in Tulsa, Oklahoma.



Tycos Taylor

Indicating · Recording · Controlling

TEMPERATURE *and* PRESSURE INSTRUMENTS

*The name Taylor now identifies our complete line of products, including Tycos instruments

6. Electrodes

METAL & THERMIT CORPORATION

Metal & Thermit Corporation, 120 Broadway, New York, announces two additions to the Murex line of mineral coated arc welding electrodes. One is a special electrode for welding Cromansil steel, a new development in high-strength steels. The electrode gives a deposit of the same analysis as Cromansil and the weld has physical properties said to be equal to the parent metal in every characteristic.

The second addition to the Murex line is an electrode which deposits a metal containing 4 to 6 per cent chrome and .5 per cent molybdenum and is especially suited for welding petroleum refining equipment where such metals are extensively used.

7. Reclosing Device

GENERAL ELECTRIC COMPANY

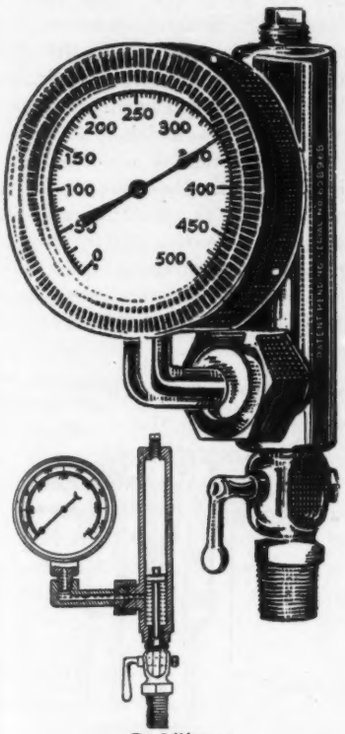
General Electric Company, Schenectady, New York, has developed a direct-acting reclosing device, designated as type SM, for use with oil circuit breakers. This device will reclose a breaker, one, two or three times, with equal time intervals between reclosures, when the breaker is tripped by overload. If the overload ceases after any reclosure, the attachment will return to its normal position and the circuit breaker will remain closed. If the overload still exists after the last reclosure, the breaker will remain locked open and it will be necessary to close it manually before any further automatic operation takes place. The attachment is a mercury-tube device in which timing is secured by running mercury through an orifice into a reclosing contact chamber. The tube has

sealed in contacts which do not deteriorate or require maintenance. The number of consecutive reclosures that the equipment will make and the time interval between reclosures are fixed during the process of manufacture. A new tube, however, can be substituted in the event a different number of reclosures or different time intervals are desirable.

8. Stabilizer

BOILER EQUIPMENT SUPPLY CO.

Boiler Equipment Supply Company, Oklahoma City, Oklahoma, announces a stabilizer to prevent oscillations of the hand movements of pressure gauges on gas and air compressors.



Stabilizer

Spirits of glycerine is used in the stabilizer to prevent sulphur and other gases from entering the springs of the gauges and to prevent freezing.

The manufacturer claims the device exposes valve trouble and that it is especially economical where more than one compressor is hooked up on the same line.

9. Rotameters

SCHUTTE & KOERTING COMPANY

Schuette & Koerting Company, Philadelphia, announces a new line of mechanical, electric and orifice type Rotameters. The Rotameter is a flow metering device used to show rates of flow of water, oil, air, gas, chemicals, and other liquids and fluids. It consists essentially of a vertical transparent tube having a tapered bore, with the small end at the bottom. Inside the tube is a top-shaped float held in suspension by the upward flow of the liquid or gas. The float is entirely free and is caused to rotate rapidly by means of specially shaped slots cut in its head against which the fluid passing through the meter impinges. The float remains in the center of the fluid stream and since it does not come in contact with the tube wall, is frictionless in operation, permitting accurate readings. The annular space between the float and tubes increases as the float is carried upward by increasing flow, and the position of the float is in direct relation to the flow and the calibration is practically a straight line. Thus the Rotameter is essentially an orifice meter in which the head on the orifice as determined by the weight of the float, remains constant and the area of the orifice varies directly as the fluid flow. Calibration is usually furnished as a curve sheet, plotting flow readings against millimeter scale readings. A direct reading capacity scale can also be etched onto the glass tube. The instrument has been finding application in the refining industry in measuring and controlling flows of sulphuric acid and caustic soda in gasoline treating and of ammonia in crude oil treating lines.

FOR HAZARDOUS LOCATIONS

G-E EXPLOSION-PROOF REFINERY MOTORS

Assure Safety, Economy, Dependability

HERE are some of the reasons why G-E totally enclosed, fan-cooled motors for Class I, Group D, locations are safe, economical, and able to stay longer on the job:

Strong, reënforced housings safely withstand internal explosions

One-piece, cast-aluminum rotors, carefully ground and balanced to eliminate vibration and maintain uniform air gap

Cartridge-type ball bearings sealed in grease for protection against dust and moisture

Motor cooled by air, fan-forced through ample passageways

Underwriters' Laboratories label; motors are tested and listed for Class I, Group D, locations as defined by the National Electric Code

Write for publication GEA-1716 on explosion-proof motors and control. Address the nearest G-E office, or General Electric, Dept. 6A-201, Schenectady, N. Y.

200-746

GENERAL ELECTRIC

10. Indicating Gauge

THE FOXBORO COMPANY

The Foxboro Company, Foxboro, Mass., announces development of a small accurate indicating gauge with a full length 270-degree scale, designated as model "DH". This gauge employs a full length Bourbon spring which results in a reduction in movement multiplication and an increase in inherent accuracy. It is said to be accurate to within one per cent of its total scale and is fully guaranteed by the makers. The gauge is finished in a drawn brass case and ring with buffed nickel finish. Buffed brass or chromium finish can be supplied. The connection may be either top, bottom or left or right side. Dials are either black background and white block figures or white background with black figures.

11. Light Weight Fittings

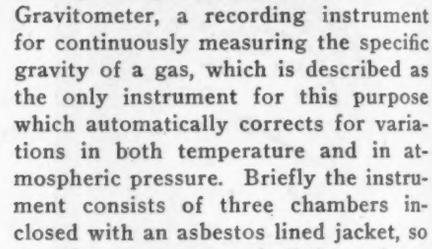
TAYLOR FORGE & PIPE WORKS

Taylor Forge & Pipe Works, Box 485, Chicago, has developed a new line of light weight fittings for use with light wall piping and Taylor spiral pipe. The fittings are fabricated from No. 10 gauge (0.134 inch) steel by welding. Die formed, they present a smooth surface with minimum resistance to flow. Center to end dimensions conform with the 125 pound American standard. They are furnished plain end or flanged, or flanged one end only. They are suitable for hydraulic pressures up to 200 pounds, and higher for the smaller sizes and are available to include ells, tees, crosses, Y's, reducers and combinations.

12. Gravity Meter

AMERICAN METER COMPANY

American Meter Company, Erie, Pennsylvania, announces the Metric Gravitometer, a recording instrument for continuously measuring the specific gravity of a gas, which is described as the only instrument for this purpose which automatically corrects for variations in both temperature and in atmospheric pressure. Briefly the instrument consists of three chambers inclosed with an asbestos lined jacket, so that the temperature of all three chambers is the same. The first chamber serves for the admission and control of the gas. The second chamber, centrally placed, is sealed, containing a definite quantity of air under a pressure of 30 inch mercury at a temperature of 60°F. The third chamber contains a pair of fans rotated by means of a constant speed motor for the measurement of the gas. In operation, gas enters through a small reducing valve where its pressure is adjusted by means of the diaphragm and valve to be exactly equal to that of the air in the sealed chamber at the temperature of operation. Gas then flows into the center of the two-stage blower from which it is expelled to a burner. The pressure differential between the inlet



Cross Section of Metric Gravitometer

"Y"

"PLUNGER RELEASE" LUBRICATED STRAIGHTWAY SPECIAL

VALVES

of

Five Different Corrosion-resisting Alloys

For Any Type of Valve Handling Corrosive Liquids, Select One of These Alloys:

DURIRON; a high-silicon iron almost universally resistant to acid corrosion. It is very hard, resists abrasion and scouring, and is of the same qualities throughout. It is practically unaffected by sulphuric, nitric, acetic, and most other commercial acids at any strength or temperature.

DURICHLOR; a silicon iron especially resistant to hydrochloric acid in all concentrations and temperatures up to the boiling point. Like Duriron, it is very resistant to abrasion and scouring.

DURIMET; a low-carbon nickel-chromium-silicon steel possessing great resistance to many corrosives, especially sulphuric acid in the lower concentrations at all temperatures. Has greater strength than mild steel.

DURCO ALLOYS, such as 18% chromium-8% nickel (KA2S), or with the addition of molybdenum (KA2SMo), and other of the more popular stainless steel analyses, are all made with a low carbon content (.07% max.) and are produced in high frequency electric induction furnaces.

ALCUMITE, a superior aluminum bronze highly resistant to sulphuric acid in the lower concentrations.

There is an alloy for handling any corrosive chemical used in the refinery. Don't throw money away by using the wrong one. Write for additional information.

THE DURIRON COMPANY, INC.

412 N. FINDLAY ST. DAYTON, OHIO

DURIRON

and outlet of the blower constitutes an exact measure of the density of the gas (and of the specific gravity since the temperature and pressure equal that of the standard). It is this differential which is recorded by the instrument.

13. Oil Heater

COEN COMPANY

Coen Company, of Los Angeles, Houston and New York City, announces an eight-pass outside joint oil heater. The company claims that with this type heater it is impossible for a leaky tube joint to permit oil entering the steam space to find its way into the boiler, hot well, or cooling tower. Tube sheets are rolled steel, two tube sheets at each end, with a space between them open to the air. Thus, any oil leak or steam leak will drain to the atmosphere. In addition, an expansion joint is built into the shell to relieve expansion strains. With the tube arrangement the cold oil goes through the center tubes and is gradually heated as it approaches the outer row nearest the casing, which is at steam temperature. With this arrangement of oil passage there is no great pressure drop to cause a short circuit or leak from one pass to another. In operation steam is admitted to a cored annular passage at either end of the shell. From this passage it is distributed into the heater shell through a row of holes on the inner circumference. There is a steam connection at either end of the heater and drain connections at four points, two at each end. The heater may be used as a cooler by reversing the oil flow through the heater and circulating cold water through the steam space. Hot oil may be rapidly cooled in this manner. The outside joint heaters are adaptable to either vertical or horizontal installation and may be installed in any multiple combination.

14. Photronic Kit

WESTON ELECTRIC INSTRUMENT CORPORATION

Weston Electrical Instrument Corporation, 614 Frelinghuysent Avenue, Newark, N. J., has announced a new, inexpensive Photronic Control Kit which is being marketed especially for engineers and manufacturers who prefer to do their own experimenting with photo-electric control for mechanical equipment, operations and for processes of various kinds.

The kit contains all the equipment necessary for the engineer to start immediate experiments, together with diagram of connections. The equipment can be used as a smoke detector, burglar alarm, turbidity detector, door opener, counter for all classes of service, safety device on machines, etc.

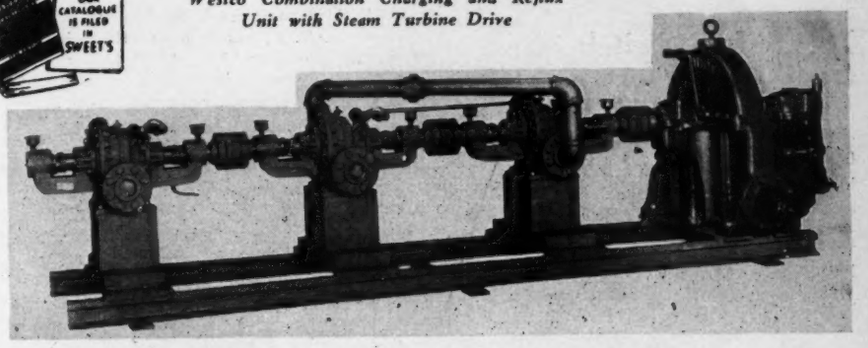
The cell included in the kit is the Weston Photronic Cell which has the faculty of transforming light energy directly into electrical energy and operates the Weston relays without the use of any auxiliary apparatus or batteries. As far as is known, the cell has unlimited life and the output is constant. Its spectral response is about the same as the human eye, so that it is extremely sensitive to color changes and is finding wide application whereever processes must be controlled by changes in color.

15. Foam Generator

PYRENE MANUFACTURING CO.

Pyrene Manufacturing Company, Newark, N. J., announces the Phonene Hopper, a continuous foam generator for converting a fire line from a continuous water stream to a continuous foam stream. The unit is coupled into a hose line, water enters one side, Phonene powder is poured into the hopper

Westco Combination Charging and Reflux Unit with Steam Turbine Drive



HIGH PUMP EFFICIENCY

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LARGE capacities. Small capacities. Westcos handle either one against high pressures—and do it with high efficiency. That's because this modern pump's application of centrifugal force *is different.* Another feature is Westco's ability to deliver multi-stage performance with only single stage construction. This naturally eliminates the necessity for costly multi-stage construction.

Westco handles light, volatile, gasoline, propane etc. of 100° to 130° A. P. I. against pressures up to 300 lbs. —and does it without vapor binding.

Wide Operating Range

Westco automatically adjusts itself to any fluctuations in the operating pressure. An even, non-pulsating flow is assured at all times. By increasing the efficiency of the towers, this characteristic makes Westco the ideal pump for feed and reflux duty on high pressure stabilizers.

Only one moving part—the Impeller, which operates *without metal-to-metal contact inside the pump chamber.* This extreme simplicity means trouble-free operation, minimized maintenance and compactness.

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Without obligation, we'll gladly send you complete details that tell how and where you can apply Westco's valuable advantages in your own Refinery or Natural Gasoline Plant. Just fill in the coupon below and *mail it today.* *WESTCO PUMP CORPORATION,* Davenport, Iowa. *Branches:* New York, Philadelphia, Chicago, Los Angeles and San Francisco. *Representatives in 50 Principal Cities.*

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WESTCO *TURBINE* PUMPS

HIGH PRESSURE - - - SINGLE STAGE

and foam is discharged through the hose line at the other side of the unit. It is designed for industrial service wherever quantities of flammable liquids are used or stored. The hopper has no levers, gauges or moving parts. The hopper and hopper bowl are cast of a special composition metal and can not be bent out of shape. It is claimed that the flow of powder is governed automatically by the pressure and amount of water available and that the device operates efficiently with water pressure as low as 35 pounds. An auxiliary water jet in the hopper erodes the powder and flushes it into the main water stream passing through the base. The unit weighs only 42 pounds.

16. Safety Switch

ELECTRIC CONTROLLER & MANUFACTURING COMPANY

Electric Controller & Manufacturing Company, 2696 East 79th Street, Cleveland, Ohio, announces a new type safety switch. Although designed for severe duty these switches are of compact construction, the over-all dimensions are small, nothing projects beyond the width of the box and the cover swings vertically, which permits of minimum mounting space. The switches are quick-make and quick-break-double-break, semi-floating V-blades (movable contacts) engage and open rapidly; they cannot be partially opened or partially closed. Steel back-up springs on the V-stationary-contacts guarantee full contact under heavy pressures. The fuse door is interlocked with the operating handle so that raising the door trips the switch and the fuses can not be reached except when the switch is open. The switch mechanism is assembled on a single base held in the box by four screws, permitting easy removal of the mechanism for inspection, replacement of parts, or substitution of a new switch. The switches are convertible from larger to small sizes simply by changing fuse clips and moving fuse block to the proper threaded holes supplied in all boxes.

Items About Manufacturers

The Superheater Company, New York, has appointed William T. Conlon, manager of its Industrial Department. In this capacity he will have charge of design, manufacture, and sales of Elesco superheaters for all types of boilers for public utility and industrial power plants, desuperheaters, resuperheaters, furnace water walls and other heat exchange apparatus for power plants.

Coppus Engineering Corporation, Worcester, Mass., has appointed John O. Weber, 122 Main Street, Louisville, Kentucky, representative for the state of Kentucky, with the exception of seven counties which will continue to be served by the company's Cincinnati office.

Worthington Pump & Machinery Corporation, Harrison, N. J., has appointed Kroeschell Engineering Company, 2306 North Knox Avenue, Chicago, as authorized dealer in the Chicago area for Worthington refrigeration equipment.

Chemical Construction Corporation, 535 Fifth Avenue, New York, has transferred the engineering department from Charlotte, North Carolina, to the New York office. The transfer was made to secure closer co-ordination between the administrative and technical departments.

J. Frederick Byers, president of Byers Pipe Company, Pittsburgh, and his son, A. McB. Byers, sailed from New York for Cherbourg, late in August.

Reading Iron Company, Philadelphia, has announced appointment of William Craig Wolfe as vice president in charge of sales.

Blaw-Knox Company, Pittsburgh, announces appointment of H. W. How, on the staff of the Process Equipment Department, to become associated with the further development of the company's extended line of welded pressure vessels and equipment for process industries.

The Hanlon group of companies, consisting of Hanlon-Buchanan, Inc., Hanlon-Waters, Inc., Hanlon-Boyle, Inc., Hanlon Gasoline Company and Henaghan & Hanlon, Inc., are moving their offices to a suite of rooms especially prepared for them in the National Bank Building, Tulsa.

Over the past six months Hanlon-Buchanan, Inc., has become financially interested in six new natural gasoline plants in the East Texas, Conroe and Refugio fields, the production from which will be utilized in their export and coastwise cargo sales through their terminals at Goodhope, Louisiana, and Houston, Texas. Four of these new plants are in operation and two under construction are to be completed about October 15. These six plants, along with plants in Breckenridge, Texas, and West Virginia, which are wholly owned by this group, will have a daily production of 145,000 gallons of natural gasoline. In addition to this, Hanlon-Buchanan, Inc., has the exclusive marketing of the production from a large number of plants in the Mid-Continent field, all of which makes this company one of the major factors in natural gasoline production as well as marketing.

This activity, along with the entry of Hanlon-Waters, Inc., into the manufacture of a complete line of automatic control equipment for all branches of the petroleum industry, has made it necessary to secure larger quarters to accommodate this growing organization.

Struthers-Wells Company, Warren, Pennsylvania, announce appointment of Kerr Machinery Corporation, Kerr Building, Detroit, Michigan, as its representative in Michigan, exclusive of the northern peninsula. National Equipment Company, Salt Lake City, Utah, was named representative in the states of Utah, Nevada, Idaho, Montana and Wyoming west of Rock Springs.

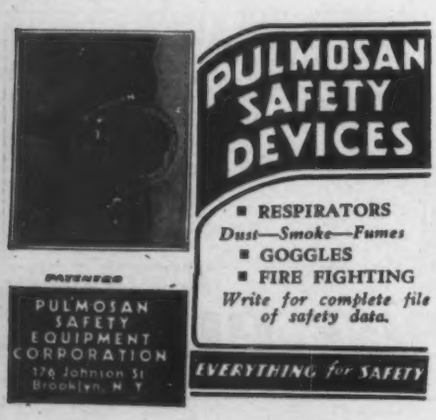
Shand & Jurs Company calls attention to an error appearing in this department, issue of July, stating that the address of the Shand & Jurs Sales Company offices are at 295 Madison Avenue, New York, instead of 225 Madison Avenue, as reported.

Fisher Governor Company, Marshalltown, Iowa, manufacturers of automatic control specialties, has announced appointment of Smith Separator Company, Box 2003, Tulsa, as sales representative handling Fisher equipment in Oklahoma and northern Texas.

Smith Separator Company is one of the oldest equipment companies, manufacturing and selling the Smith oil and gas separator. This organization has had many years experience in the sale and service of Fisher controls and is in position to service the users of Fisher equipment in an outstanding manner.

In addition to several sales engineers in the regular Smith organization, C. D. Peterson, who has had nine years experience in the design, operation, and service of automatic controls at the Fisher factory, will be permanently located in Tulsa, to offer even greater service in a technical manner.

In making this announcement, J. H. Fisher, president of Fisher Governor Company, asserts that the desire to better serve the petroleum industry in the Mid-Continent field is the basis for this new sales plan and that the increased sales of Fisher equipment warrants this improved service.



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